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NASA Contractor Report 178176

EVALUATION OF HIGH TEMPERATURE STRUCTURAL ADHESIVES FOR EXTENDED SERVICE - PHASE V

C. L. Hendricks, S. G. Hill, J. N. Hale, and W. G. Dumars

Boeing Aerospace Company
Seattle, Washington 98124

Contract NAS1-15605
February 1987

NASA
National Aeronautics and
Space Administration

Langley Research Center
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FOREWORD

This report describes the work accomplished under Contract NAS1-15605, Phase V, "Evaluation of High Temperature Structural Adhesives for Extended Service". The contract was sponsored by the National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia 23665-5225.

Mr. Paul M. Hergenrother was NASA Technical Monitor. The Materials and Processes Technology organization of the Boeing Aerospace Company (BAC) was responsible for the work performed in Phase V. Mr. Carl L. Hendricks was Program Manager. Mr. Sylvester G. Hill was Technical Leader and Mr. Jeremy N. Hale and Mr. William C. Dumars were co-principal investigators. The following personnel provided critical support to the various program activities.

Ralph E. Hodges	Adhesive Film Preparation
Arlene McKeeman Brown	Composites and Adhesives Group Leader
Thomas F. Terbilcox	Materials and Processes Engineer

Use of commercial products or manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration or The Boeing Company.

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1.0 SUMMARY AND INTRODUCTION

1.1 Summary

This report documents the work performed by the Boeing Aerospace Company for the National Aeronautics and Space Administration, Langley Research Center, under contract NAS1-15605, Phase V. The primary objective of this program was to evaluate three experimental polymers as high temperature structural adhesives for bonding 6Al-4V titanium and 17-7 PH stainless steel for long-term applications at 505K (450°F). The three experimental polymers were polyphenylquinoxaline (PPQ), polyimide (STPI/LaRC-2), and polyarylene ether (PAE SO_2). A fourth polymer, LaRC-TPI, was evaluated as an adhesive for titanium honeycomb sandwich bonding. Surface preparations for the metal adherends were 10 volt chromic acid anodize and Pasa-Jell 107 for titanium, and 2 volt sulfuric acid anodize for the stainless steel.

The test matrix for evaluating the experimental adhesives consisted of metal-to-metal titanium lap shear, crack extension, and climbing drum peel specimens tested initially at temperatures ranging from 219K (-65°F) to 505K (450°F). Durability was determined as a function of strength retention after exposure to a variety of aerospace vehicle environments. These included humidity exposure (332K (120°F)/95% R.H.) for 1,000 hours, high temperature exposure (450K (350°F) and 505K (450°F)) for up to 3,000 hours, and stressed exposure to hydraulic fluid (Skydrol). Durability of bonded stainless steel joints was determined on an abbreviated test matrix.

PPQ and STPI/LaRC-2 polymers maintained structural durability in all test environments. Shear strengths at elevated temperatures did show a loss in performance due to thermoplastic yielding of the adhesives. However, this type of failure occurred at relatively high loads and no creep was recorded when stressed at 25% of ultimate strength during exposure to the same high temperatures. PAE SO_2 exhibited the lowest performance of the polymers evaluated, though maintained structural integrity in all test environments except Skydrol. Lap shear specimens from this system when stressed in Skydrol failed adhesively after less than 625 hours of exposure.

The original test plan for evaluating LaRC-TPI adhesive consisted of metal honeycomb sandwich flatwise tension, edgewise compression, short beam shear, and climbing drum

peel specimens. Since the LaRC-TPI bonded titanium sandwich panels did not meet the minimum strength requirements for flatwise tensile, testing was terminated early in the evaluation. Instead, work to improve LaRC-TPI adhesive film quality, fillet formation, and titanium honeycomb core filleting/roller coating methods was performed. LaRC-TPI powder was also evaluated as a filleting material and as an ingredient in the LaRC-TPI adhesive film. The flatwise tensile strength results for the titanium honeycomb sandwich fabricated using a combination of LaRC-TPI resin and powder were very promising.

1.2 Introduction

The advancement in aerospace vehicle designs with continuing increases in performance requirements, especially high velocity, has resulted in greater demands for structural efficiency with elevated temperature stability. These demands can, in many cases, be satisfied by adhesive bonding of structural elements. Basic development of high temperature stable adhesives remains as one of the critical technologies yet to be advanced to the stage that it can adequately support design for advanced aerospace vehicle systems. Polymer systems such as polyphenylquinoxaline (PPQ), polyimide (PI), and polyarylene ether (PAE S02) are under evaluation for potential use as adhesives in hostile thermal environments.

The objective of this program was to evaluate and test high temperature stable polymers as adhesives for extended elevated temperature service. Three experimental polymers supplied by NASA-Langley Research Center and one commercially produced polymer purchased from Mitsui Toatsu Chemicals were evaluated.

The basic approach to this study was to convert the NASA and commercial polymers to usable thin adhesive films by impregnating style 112 E-glass (A1100 finish). Titanium (6Al-4V) or stainless steel (17-7 PH) adherends were surface treated using Pasa-Jell 107, chromic acid or sulfuric acid anodization processes. Metal-to-metal and honeycomb sandwich panels were fabricated, subjected to various environmental exposures, then tested according to appropriate test matrices. The program plan included testing at temperatures from 219K (-65^{o}F) to 505K (450^{o}F), exposure to humidity, and exposure to hydraulic fluid (Skydrol).

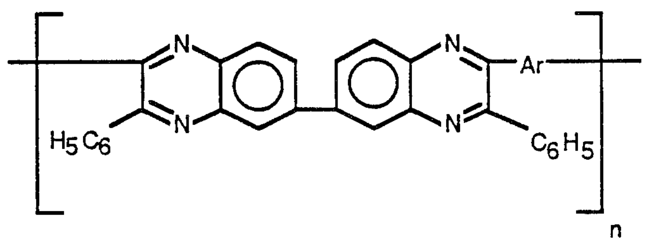
2.0 TECHNICAL DISCUSSION

This section describes the detailed technical effort that was conducted during Phase V of this program.

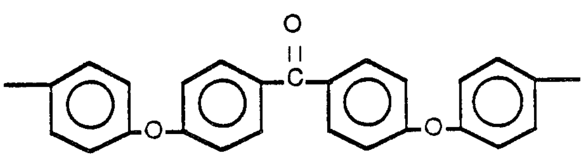
2.1 Adhesive Resin Candidate Selection

The experimental polymer candidates for metal-to-metal bond evaluation were selected in cooperation with NASA personnel. The polymers selected were: polyphenylquinoxaline (PPQ), polyimide (STPI/LaRC-2), and a polyarylene ether (PAE SO_2). The chemical structure of each polymer system evaluated is shown below.

Polyphenylquinoxaline (PPQ)



where Ar = equivalent amounts of



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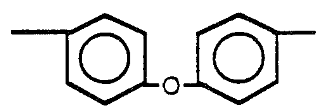
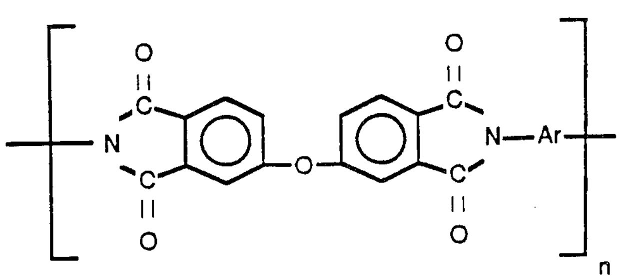
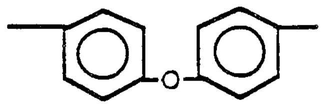


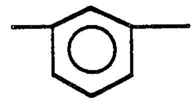
Polyimide (STPI/LaRC-2)



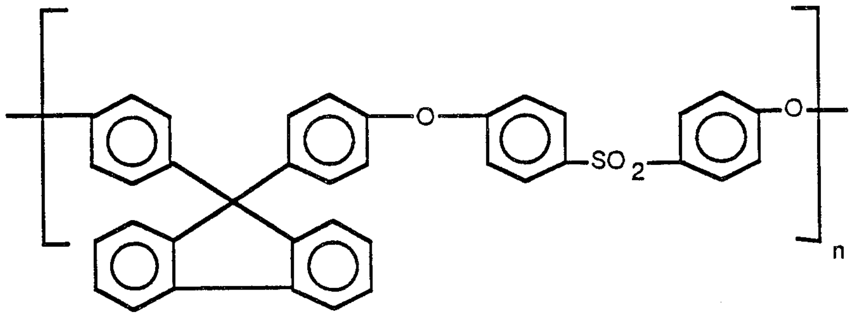
where Ar = equivalent amounts of



and

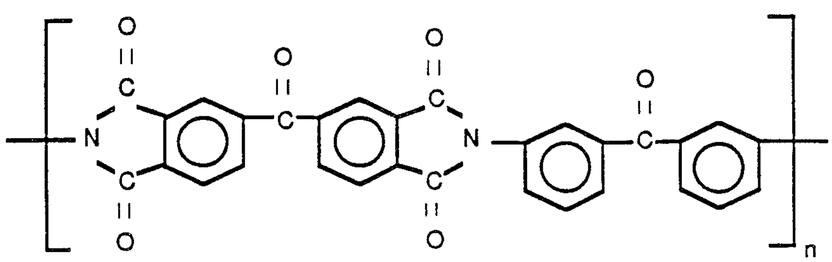


Polyarylene ethers (PAE SO_2)



The polymer candidate for honeycomb sandwich bond evaluation, a commercially produced polyimide from Mitsui Toatsu Chemicals (LaRC-TPI), was also selected in cooperation with NASA personnel. The chemical structure of this polymer is shown below.

Polyimide (LaRC-TPI)



(non-aniline terminated)

Each polymer was characterized upon receipt for percent resin solids, inherent viscosity, and the temperature range of volatile evolution. These results are presented in Table 2.1.1.

Table 2.1.1

CHARACTERIZATION OF CANDIDATE POLYMER SOLUTIONS

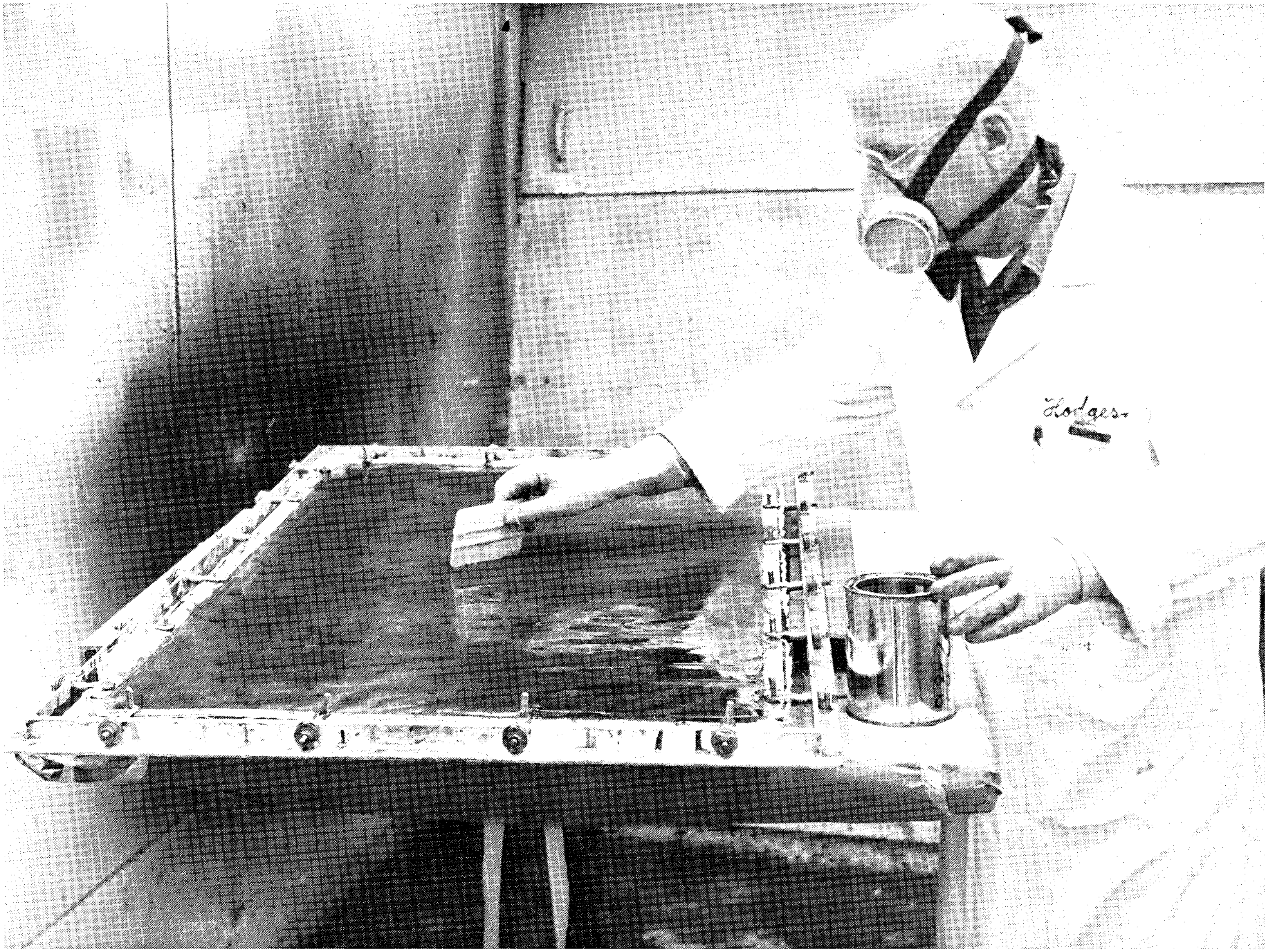
POLYMER	SOLVENT SYSTEM	SOLIDS CONTENT	INHERENT * VISCOSITY	TEMPERATURE OF SOLVENT EVOLUTION
Polyphenyl-quinoxaline (PPQ)	1:1 mixture of m-cresol and xylene	20%	0.57 dl/g	413K (284°F) to 483K (410°F)
Polyamide Acid of Polyimide (STPI/LaRC-2)	Diglyme	17.5%	0.46 dl/g	385K (185°F) to 468K (383°F)
Polyarylene Ether (PAE SO_2)	N,N Dimethyl-acetamide	15%	0.40 dl/g	433K (338°F) to 483K (410°F)
Polyamide Acid of Polyimide (LaRC-TPI)	Diglyme	34%	0.48 dl/g	414K (285°F) to 478K (400°F)

* Measurement of a 0.5% solids solution in the appropriate solvent system at 35°C.

2.2 Preparation of Adhesive Films

Each of the polymers was processed into adhesive film by impregnating Style 112 E-glass (A1100 finish) with the polymer solution. Prior to processing, the glass fabric was oven dried to remove any residual moisture and stretched tightly on aluminum frames to facilitate processing.

A dilute adhesive solution (approximately 3 parts appropriate solvent system to 1 part supplied polymer solution) was applied by brush to the fabric and air dried. Additional coats of the undiluted, unfilled polymer solution were applied by use of a plastic sweep to alternating sides of the fabric until the desired film thickness of 0.25 to 0.35 mm (0.010 to 0.014 in) was achieved. The glass support frame and application technique are shown in photograph 2.2.1. After the first thin coat, the remaining individual coats were oven dried from 338K to 450K (150°F to 350°F) in 30 minutes/10K (50°F) increments. LaRC-TPI required a higher drying temperature (477K (450°F)). This



Photograph 2.2.1 — Preparation of Glass Supported Adhesive Films

temperature reduced the film volatiles to an acceptable level, but did not advance the resin to the point that adhesive flow was significantly reduced.

Adhesive film processing characteristics, volatile content, and flow properties were determined. The film volatile content was measured gravimetrically before and after exposure to 616K (650°F) for 30 minutes. Resin flow was measured after exposure to the appropriate cure cycle to determine its ability for flow, leveling, and wetting. Flow properties were determined by placing a 35.6 mm (1.4 inch) diameter adhesive film between Kapton film and press curing the assembly. Typical film characteristics for each system are shown in Table 2.2.1.

TABLE 2.2.1

ADHESIVE FILM CHARACTERISTICS

Adhesive	Film Volatiles	Flow Test (% increase in diameter)
Polyphenylquinoxaline	0.5%	4.0%
Polyimide (STPI/LaRC-2)	0.5%	2.0%
Polyarylene Ether (PAE SO_2)	0.5%	3.0%
Polyimide (LaRC-TPI) *	1.5%	—

* 477K (400°F) maximum drying temperature

2.3 Preparation of Metal-to-Metal Test Specimens

The adherends for study in this phase were 6Al-4V titanium and 17-7 PH stainless steel. Three types of metal-to-metal titanium test specimens were prepared; single lap shear, crack extension, and climbing drum peel. The configuration of each specimen is shown in Figure 2.3.1. Titanium adherend surface preparation was chromic acid anodize (10 volt CAA), per Boeing Process Specification BAC 5890, or Pasa-Jell 107 as specified by NASA-Langley. The general details of these titanium surface preparations are as follows.

Chromic Acid Anodize:

- o Vapor degrease
- o Alkaline clean, 10 min.

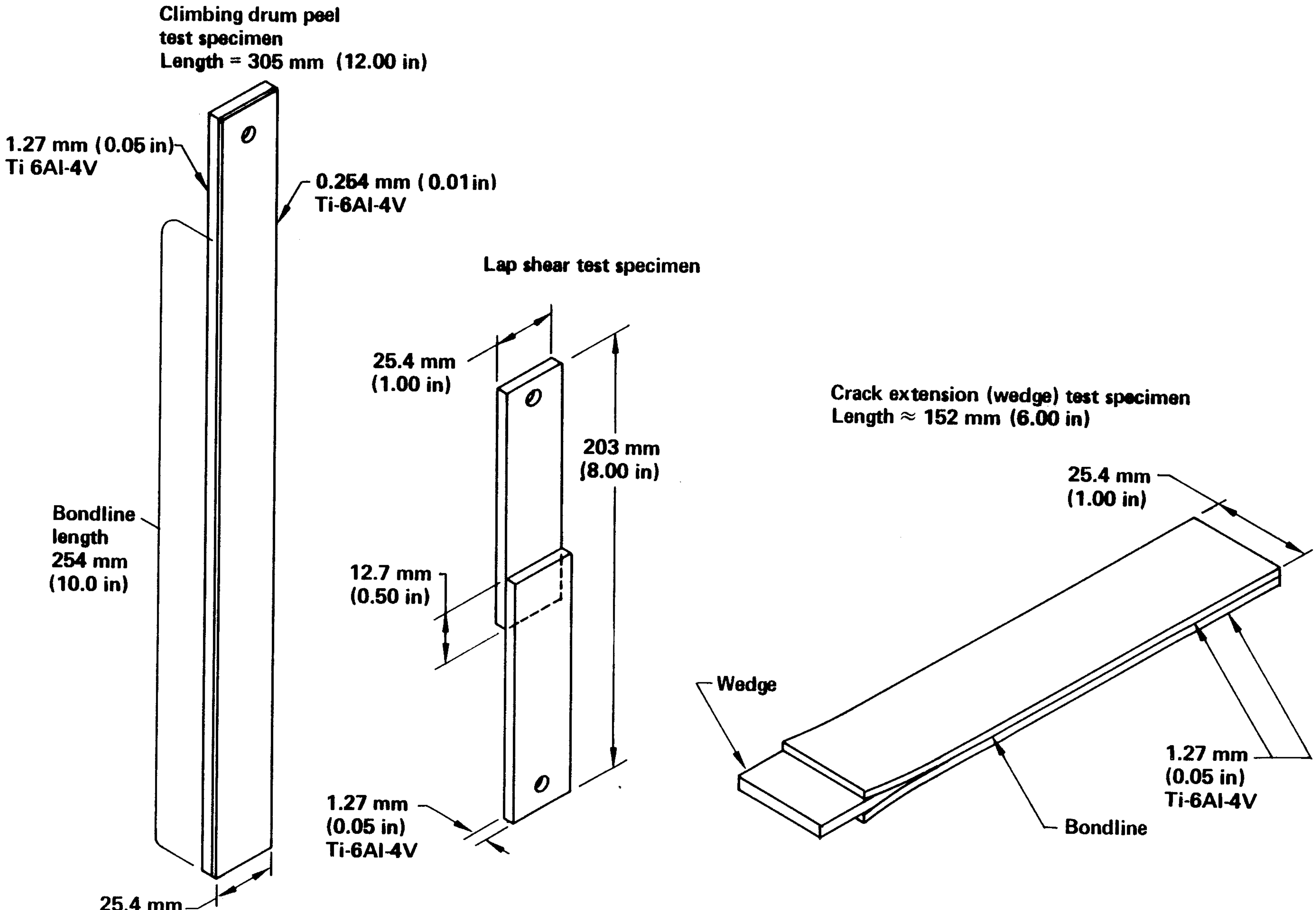


Figure 2.3.1 Metal—to—Metal Mechanical Test Specimen

- o Rinse hot water, 10 min.
- o Nitric-hydrofluoric acid etch, 90 sec.
- o Rinse cold water, 10 min.
- o 10 volt CAA, 20 min.
- o Rinse cold water, 10 min.
- o Air dry at 344K (160°F)
- o Prime with appropriate primer within 72 hours

Pasa-Jell 107:

- o Methanol wash
- o "Sand blast" with 100 mesh alumina in a pressure blasting 80 psi apparatus
- o Methanol wash
- o Dip in Pasa-Jell 107, 1 min.
- o Remove and allow to etch, 10 min.
- o Redip in Pasa-Jell 107, 1 min.
- o Remove and allow to etch, 10 min.
- o Rinse hot water, 5 min.
- o Suspend in an ultrasonic water bath (tap water), 5 min.
- o Air dry, 5 min.
- o Ultrasonic water bath (de-ionized water), 5 min.
- o Air dry at room temperature, 10 min.
- o Heat coupons in 343K (158°F) oven, 10 min.
- o Prime with appropriate primer within 4 hours.

Surface preparation for 17-7 PH stainless steel was a 2 volt sulfuric acid anodize developed by Boeing. The general details of this surface preparation technique are as follows.

- o Vapor degrease
- o Alkaline clean, 10 min.
- o Rinse hot water, 5 min.
- o 2 volt SAA, 5 min., at 316K (110°F)
- o Rinse cold water, 10 min.
- o Air dry, 344K (160°F)
- o Prime with appropriate primer within 72 hours.

Panels 0.09 m^2 (1 ft^2) of 1.27 mm (nominal 0.050 inch) thick stainless steel were surface treated in this manner.

Immediately after surface preparation, each set of 6Al-4V titanium or 17-7 PH stainless steel panels were primed with a dilute solution of the appropriate adhesive and oven dried at 435K (325°F) for one hour. The test specimens were assembled by cutting appropriate sized pieces of film, assembling the adherends and film in the bonding jigs, and vacuum bagging with Kapton film. Autoclave cure for the metal-to-metal test specimens was performed according to the following schedules:

- PPQ
  1. Apply vacuum and 1.38 MPa (200 psi) autoclave pressure.
  2. Heat to 644K (700°F) at 3K (5°F)/minute.
  3. Hold at 644K (700°F) for 60 minutes.
  4. Cool to below 338K (150°F) before releasing pressure.

- STPI/LaRC-2
  1. Apply vacuum and 1.38 MPa (200 psi) autoclave pressure.
  2. Heat to 616K (650°F) at 3K (5°F)/minute.
  3. Hold at 616K (650°F) for 90 minutes.
  4. Cool to below 338K (150°F) before releasing pressure.

- PAE SO_2
  1. Apply vacuum and 0.69 MPa (100 psi) autoclave pressure.
  2. Heat to 616K (650°F) at 3K (5°F)/minute.
  3. Hold at 616K (650°F) for 15 minutes.
  4. Cool to below 338K (150°F) before releasing pressure.

- LaRC-TPI (Process Control Specimens for Honeycomb Bonding)
  1. Apply vacuum and 1.38 MPa (200 psi) autoclave pressure.
  2. Heat to 616K (650°F) at 3K (5°F)/minute.
  3. Hold at 616K (650°F) for 90 minutes.
  4. Cool to below 338K (150°F) before releasing pressure.

The test matrix presented in Table 2.3.1 applies to the following:

- PPQ, 6Al-4V Ti, 10 volt CAA
- PPQ, 6Al-4V Ti, Pasa-Jell 107
- STPI/LaRC-2, 6Al-4V Ti, 10 volt CAA
- PAE SO_2, 6Al-4V Ti, 10 volt CAA

TABLE 2.3.1

EXPERIMENTAL POLYMER: TEST MATRIX

METAL-TO-METAL TEST SPECIMENS *

Test Condition	Lap Shear, MPa (psi)	Crack Extension, mm (inches)	Climbing Drum Peel, N·M (in·lb)
Ambient Initial	5	4	4
219 K (-65°F) Initial	5	-	-
450 K (350°F) Initial	5	4	4
505 K (450°F) Initial	5	4	-
Ambient after exposure to 322 K (120°F)/95% R.H. 1000 hrs.	5	4	4
450 K (350°F) after exposure to 322 K (120°F)/95% R.H. 1000 hrs.	5	4	-
Ambient after exposure to Skydrol at ambient stressed to 25% of ultimate. 1000 hrs.	5	-	-
450 K (350°F) after exposure to Skydrol at ambient stressed to 25% of ultimate. 1000 hrs.	5	-	-
450 K (350°F) after exposure to 450 K (350°F) in a air.			
1000 hrs.	5	4	-
3000 hrs.	5	#	-
505 K (450°F) after exposure to 505 K (450°F) in air.			
1000 hrs.	5	4	-
3000 hrs.	5	#	-
450 K (350°F) stressed at 25% of ultimate to determine creep resistance 3000 hrs.	5	-	-
505 K (450°F) stressed at 25% of ultimate to determine creep resistance 3000 hrs.	5	-	-

* Number of specimens tested at each condition.

\# Crack extension specimens examined after 1000 and 3000 hours exposure.

2.4 Metal-to-Metal Bond Test and Analysis

The performance of the experimental polymers as metal-to-metal adhesives was determined through single lap shear, crack extension, and climbing drum peel tests.

Preliminary screening of the experimental polymers was completed on titanium single lap shear specimens at 450K (350°F) and 505K (450°F) test temperatures. All candidates were required to meet or exceed minimum shear strength requirements of 24.1 MPa (3500 psi) at 450K (350°F) and 20.7 MPa (3000 psi) at 505K (450°F).

2.4.1 Lap Shear Strength Test and Analysis

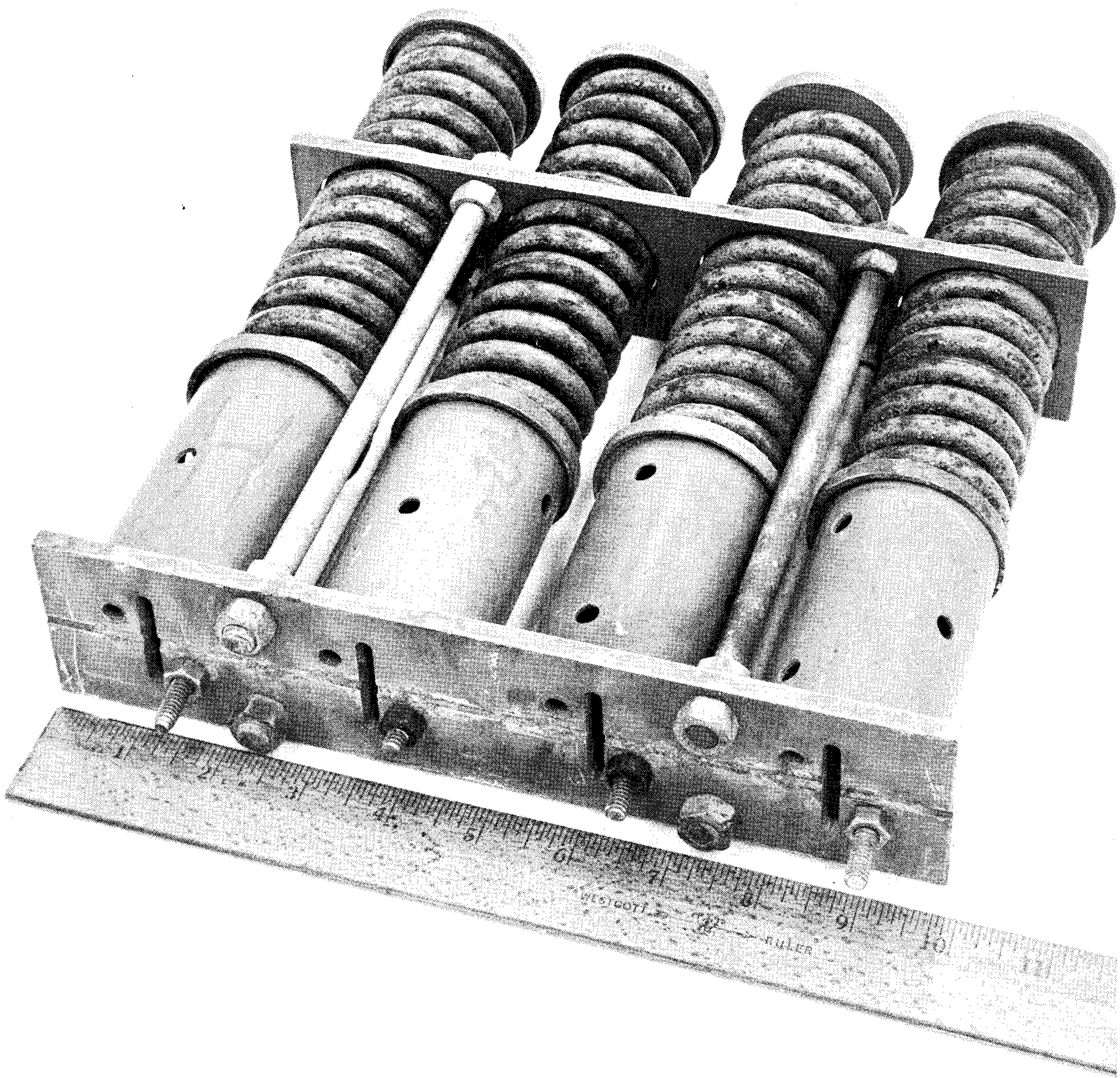
Single lap shear strength was determined at ambient temperature, 219K (-65°F), 450K (350°F), and 505K (450°F), after a 10 minute exposure at each temperature. This provided information regarding the strength at each temperature, and a baseline for further exposures. These exposures included unstressed aging at 450K (350°F), 505K (450°F), and 322K (120°F)/95% relative humidity. Stressed specimens were exposed at 25% of ultimate strength at 450K (350°F), 505K (450°F), and in Skydrol at 298K (75°F).

Stressed specimens were exposed using the apparatus shown in photograph 2.4.1.1. The four springs were compressed to the mean load of the lap shear strength for the given test temperature using a calibrated testing machine, and the specimens were secured in the fixture. The mean load was distributed over four springs at 25% of ultimate strength for each specimen.

A summary of lap shear strengths for PPQ, STPI/LaRC-2, and PAE SO_2 are presented in Figures 2.4.1.1 and 2.4.1.2. This information is also presented in Tables 2.4.1.1 through 2.4.1.4. The individual specimen data is available in the Appendix.

PPQ/Chromic Acid Anodize Surface Preparation

The performance of PPQ adhesive on chromic acid anodized titanium exhibited results consistent with those of previous years ("Evaluation of High Temperature Structural Adhesives for Extended Service,", Phases I through IV). Although the performance was very good at ambient temperature, a considerable decrease in strength occurred at the initial tests of 450K (350°F) and 505K (450°F). Strengths decreased to 24.9 MPa (3610



Photograph 2.4.1.1 – Static Tensile Stress Apparatus

FIGURE 2.4.1.1
EFFECT OF TEMPERATURE ON ADHESIVE LAP-SHEAR STRENGTH
ADHEREND: 6AL-4V TITANIUM

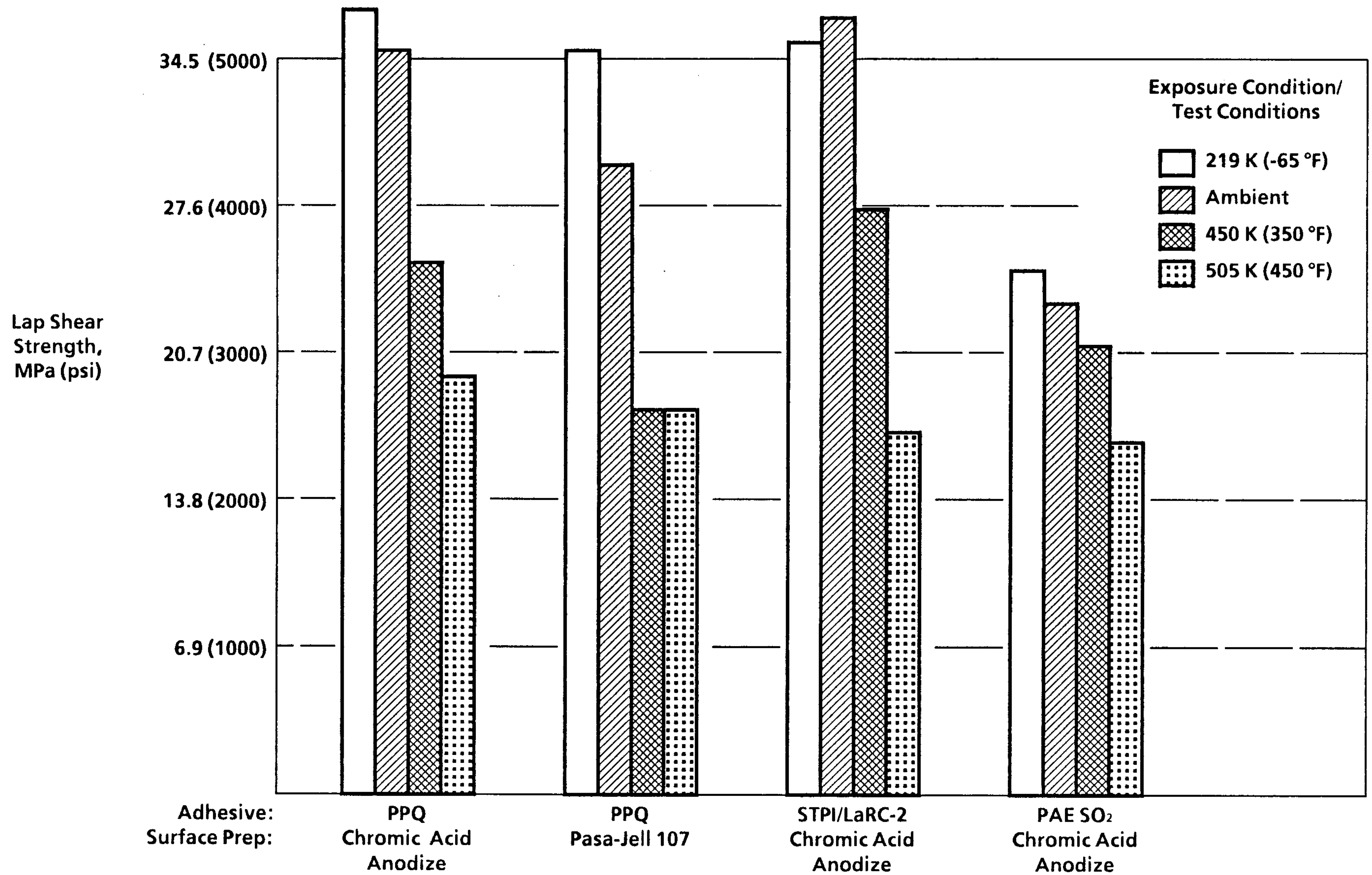


FIGURE 2.4.1.2
EFFECT OF HUMIDITY EXPOSURE ON LAP-SHEAR STRENGTH (1000 HOUR EXPOSURE) ADHEREND: 6AL-4V TITANIUM

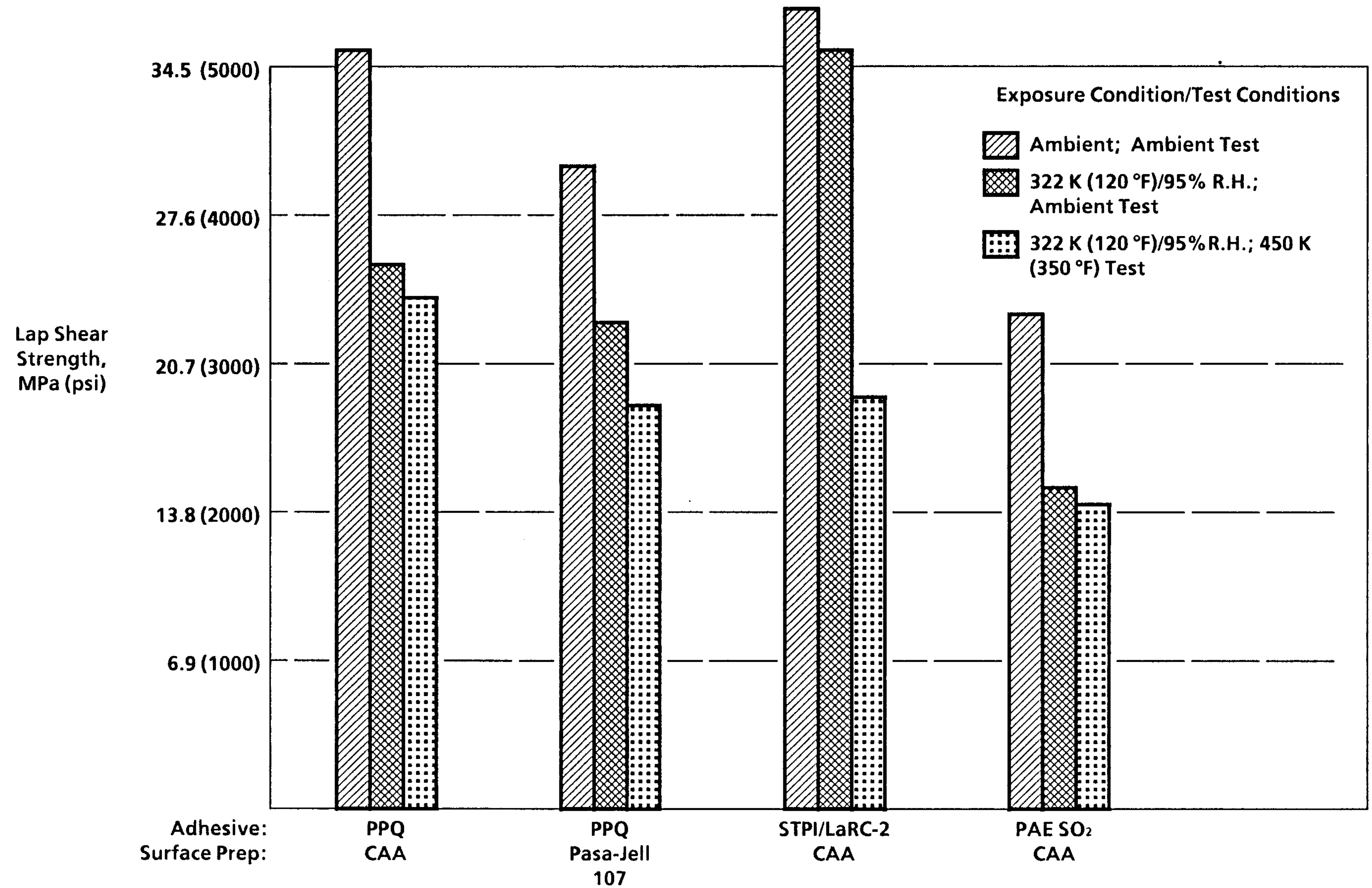


TABLE 2.4.1.1

DATA SUMMARY: PPQ ADHESIVE (MEAN TEST VALUES)

ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - 10 VOLT CHROMIC ACID ANODIZE

Test Condition	Lap Shear, MPa	(psi)	Crack Extension, mm	(inches)	Climbing Drum Peel, N·M	(in·lb)
219K (-65°F) Initial	37.0	(5370)				
Ambient Initial	35.0	(5080)	21.3	(0.84)	1.1	(9.5)
450K (350°F) After Exposure to 450K (350°F) in air						
Initial	24.9	(3610)	21.6	(0.85)	2.8	(25.0)
1000 Hours	26.8	(3880)	23.6	(0.93)		
3000 Hours	22.8	(3300)	23.6	(0.93)		
450K (350F) Stressed at 25% of Ultimate to Determine Creep Resistance						
3000 Hours	N					
505K (450°F) After Exposure to 505K (450°F) in air						
Initial	19.6	(2840)	21.8	(0.86)		
1000 Hours	21.3	(3090)	23.9	(0.94)		
3000 Hours	19.3	(2800)	28.4	(1.12)		
505K (450°F) Stressed at 25% of Ultimate to Determine Creep Resistance						
3000 Hours	N					
Ambient After Exposure to 322K (120°F)/95% R.H.						
Initial	35.0	(5080)	20.6	(0.81)	1.1	(9.5)
1000 Hours	25.4	(3690)	24.6	(0.97)	0.8	(7.0)
450K (350°F) After Exposure to 322K (120°F/95% R.H.						
Initial	24.9	(3610)	21.3	(0.84)		
1000 Hours	24.1	(3500)	25.1	(0.99)		
Ambient After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate						
Initial	35.0	(5080)				
1000 Hours	31.3	(4540)				
450K (350°F) After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate						
Initial	24.9	(3610)				
1000 Hours	19.2	(2780)				

N - No creep recorded after 3000 hours exposure

TABLE 2.4.1.2

DATA SUMMARY: PPQ ADHESIVE

ADHEREND - 6AL-4V TITANIUM (MEAN TEST VALUES)
SURFACE PREPARATION - PASA-JELL

Test Condition	Lap Shear, MPa (psi)	Crack Extension, mm (inches)	Climbing Drum Peel, N·M (in·lb)
219K (-65°F) Initial	35.0 (5070)		
Ambient Initial	29.9 (4330)	20.3 (0.80)	2.5 (22.0)
450K (350°F) After Exposure to 450K (350°F) in air			
Initial	18.2 (2640)	21.1 (0.83)	3.1 (27.0)
1000 Hours	21.4 (3110)	22.6 (0.89)	
3000 Hours	22.8 (3300)	22.6 (0.89)	
450K (350F) Stressed at 25% of Ultimate to Determine Creep Resistance			
3000 Hours	N		
505K (450°F) After Exposure to 505K (450°F) in air			
Initial	18.5 (2680)	21.6 (0.85)	
1000 Hours	14.8 (2140)	23.4 (0.92)	
3000 Hours	15.4 (2240)	23.4 (0.92)	
505K (450°F) Stressed at 25% of Ultimate to Determine Creep Resistance			
3000 Hours	N		
Ambient After Exposure to 322K (120°F)/95% R.H.			
Initial	29.9 (4330)	21.3 (0.84)	2.5 (22.0)
1000 Hours	22.8 (3310)	27.9 (1.10)	1.5 (13.0)
450K (350°F) After Exposure to 322K (120°F/95% R.H.			
Initial	18.2 (2640)	20.8 (0.82)	
1000 Hours	19.2 (2790)	27.9 (1.10)	
Ambient After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate			
Initial	29.9 (4330)		
1000 Hours	29.0 (4210)		
450K (350°F) After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate			
Initial	18.2 (2640)		
1000 Hours	12.5 (1810)		

N - No creep recorded after 3000 hours exposure

TABLE 2.4.1.3

DATA SUMMARY: STPI/LaRC-2 ADHESIVE (MEAN TEST VALUES)

ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - 10 VOLT CHROMIC ACID ANODIZE

Test Condition	Lap Shear, MPa (psi)	Crack Extension, mm (inches)	Climbing Drum Peel, N·M (in·lb)
219K (-65°F) Initial	35.4 (5130)		
Ambient Initial	36.8 (5340)	25.0 (0.98)	3.0 (26.6)
450K (350°F) After Exposure to 450K (350°F) in air			
Initial	27.5 (3990)	23.9 (0.94)	2.7 (24.1)
1000 Hours	24.1 (3490)	26.4 (1.04)	
3000 Hours	25.3 (3660)	26.4 (1.04)	
450K (350F) Stressed at 25% of Ultimate to Determine Creep Resistance			
3000 Hours	N		
505K (450°F) After Exposure to 505K (450°F) in air			
Initial	17.4 (2530)	22.6 (0.89)	
1000 Hours	19.3 (2800)	25.9 (1.02)	
3000 Hours	16.6 (2410)	27.4 (1.08)	
505K (450°F) Stressed at 25% of Ultimate to Determine Creep Resistance			
3000 Hours	N		
Ambient After Exposure to 322K (120°F)/95% R.H.			
Initial	36.8 (5340)	21.8 (0.86)	3.0 (26.6)
1000 Hours	35.1 (5090)	31.0 (1.22)	1.4 (12.2)
450K (350°F) After Exposure to 322K (120°F/95% R.H.			
Initial	27.5 (3990)	23.1 (0.91)	
1000 Hours	19.4 (2820)	33.0 (1.30)	
Ambient After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate			
Initial	36.8 (5340)		
1000 Hours	32.2 (4670)		
450K (350°F) After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate			
Initial	27.5 (3990)		
1000 Hours	24.5 (3550)		

N - No creep recorded after 3000 hours exposure, however three test specimens failed after 1650 hours possibly attributable to an oven malfunction.

TABLE 2.4.1.4

DATA SUMMARY: PAE SO_2 ADHESIVE (MEAN TEST VALUES)

ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - 10 VOLT CHROMIC ACID ANODIZE

Test Condition	Lap Shear, MPa (psi)	Crack Extension, mm (inches)	Climbing Drum Peel, N·M (in·lb)
219K (-65°F) Initial	25.0 (3620)		
Ambient Initial	23.3 (3380)	23.6 (0.93)	1.8 (16.1)
450K (350°F) After Exposure to 450K (350°F) in air			
Initial	21.2 (3070)	22.9 (0.90)	1.8 (16.1)
1000 Hours	22.1 (3210)	23.9 (0.94)	
3000 Hours	20.8 (3010)	23.9 (0.94)	
450K (350°F) Stressed at 25% of Ultimate to Determine Creep Resistance			
3000 Hours	N		
505K (450°F) After Exposure to 505K (450°F) in air			
Initial	16.8 (2440)	23.9 (0.94)	
1000 Hours	17.9 (2590)	26.2 (1.03)	
3000 Hours	16.0 (2320)	26.2 (1.03)	
505K (450°F) Stressed at 25% of Ultimate to Determine Creep Resistance			
3000 Hours	N		
Ambient After Exposure to 322K (120°F)/95% R.H.			
Initial	23.3 (3380)	23.4 (0.94)	1.8 (16.3)
1000 Hours	15.3 (2220)	28.4 (1.12)	1.9 (16.8)
450K (350°F) After Exposure to 322K (120°F/95% R.H.			
Initial	21.2 (3070)	24.4 (0.96)	
1000 Hours	14.5 (2110)	29.7 (1.17)	
Ambient After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate			
Initial	23.3 (3380)		
1000 Hours	F		
450K (350°F) After Exposure to Skydrol at Ambient. Stressed to 25% of Ultimate			
Initial	21.2 (3070)		
1000 Hours	F		

N - No creep recorded after 3000 hours exposure
F - all stressed Skydrol specimens failed in 625 hours exposure or less

psi) and 19.6 MPa (2840 psi) for 450K (350°F) and 505K (450°F), respectively. These represent a 29 and 44 percent decrease, which are consistent with previous results, but still indicate a good retention of structural integrity. Associated with the increase with temperature, was an increase in the percent of cohesive failure. This type of performance could be explained by the fact that the elevated test temperatures were beginning to approach the glass transition temperature (Tg) of the PPQ polymer (i.e., 536K (505°F)). As the Tg of a polymer is approached, and surpassed, the mechanical properties change from that of elastic strain (characteristic of the glassy region), to viscoelastic strain (characteristic of the Maxwell-Voigt element), and finally to that of viscous (plastic) flow at extremely high temperatures. The polymer, at elevated test temperatures, has a thermoplastic yield point where permanent deformation occurs in response to an applied load.

No definite trend has been established in relation to long-term exposure to elevated temperature. The degree of scatter of data points makes it difficult to determine if the thermal environment is degrading the strength of the adhesive. Although from Phase I and II studies PPQ would be expected to exhibit good stability to 505K (450°F).

Studies of the creep resistance of PPQ at elevated temperatures would tend to support the above viscoelastic response explanation. After 3,000 hours of exposure to both 450K (350°F) and 505K (450°F) no permanent displacement was recorded. The applied load and temperature was not sufficient to reach the thermoplastic yield point of the polymer.

Exposure for 1,000 hours in humidity (322K (120°F)/95% R.H.) appears to affect lap shear strength; however, the magnitude of its influence is considerably less than that of elevated temperature. When tested at ambient after humidity exposure, lap shear strengths decreased to 25.4 MPa (3690 psi) which represents a 27% decrease from the initial value. When tested at 450K (350°F) after humidity exposure, the shear strength decreased to 24.1 MPa (3500 psi) which represented only a 3% strength loss. These would still be considered structural quality bonds, but the extent of their durability over longer times would have to be determined. Structural quality bonds are generally defined as those which exceed 12.4 MPa (1800 psi) lap shear, in a cohesive failure mode.

Skydrol would appear to be the least influential factor in shear strength durability. However, the combined effect of stressed Skydrol with elevated temperature (450K

(350°F)) appears to be significant. After stressed exposure (25% of ultimate for the given test temperature) at ambient and 450K (350°F), lap shear strengths dropped to 31.3 MPa (4540 psi) and 19.2 MPa (2780 psi), respectively. These represent 11 and 23 percent strength losses from the initial values. The Skydrol exposure may be influential in degrading the adhesive/adherend interface, since a decrease in percent cohesive failure was observed at the 450K (350°F) test temperature.

PPQ/Pasa-Jell 107 Surface Preparation

PPQ adhesive on Pasa-Jell 107 treated titanium exhibited results consistent to those of PPQ on CAA treated titanium. A similar viscoelastic effect appears to influence elevated temperature performance. Lap shear values, upon exposure to 450K (350°F) and 505K (450°F), dropped to 18.2 MPa (2640 psi) and 18.5 MPa (2680 psi), respectively. The increase in percent cohesive failure was not as great as for PPQ on CAA surfaces, but an increase was evident. Despite these strength losses, this adhesive system still exhibits good structural integrity.

Similar to PPQ on CAA titanium, a trend in long-term performance after exposure to elevated temperatures does not appear to exist from the data generated at this time. Thermal stability should be very good as indicated from Phase I and II evaluation studies.

Creep resistance studies continue to support the viscoelastic/yield point explanation for adhesive performance (i.e., stress is not sufficient to reach the yield point for the adhesive at its use temperature). As on CAA treated titanium, no creep was recorded after 3,000 hours of exposure to 450K (350°F) and 505K (450°F) temperatures with 25% of ultimate strength applied.

Humidity exposure produced nearly identical results to those of PPQ on CAA treated titanium. Testing after exposure resulted in values of 22.8 MPa (3310 psi) and 19.2 MPa (2790 psi) for ambient and 450K (350°F), respectively. These correspond to a 24% decrease for specimens tested at ambient, but no change for the 450K (350°F) samples. These would be considered structural quality joints but further consideration must be given to their long-term durability.

One thousand hours of stressed exposure to Skydrol resulted in strengths of 29.0 MPa (4210 psi) and 14.5 MPa (2100 psi) at ambient and 450K (350°F) test temperatures,

respectively. The strength retention was significantly lower for stressed Skydrol specimens tested at 450K (350°F) than at ambient. The shear strengths and percentages of cohesive failure have decreased to a point where structural integrity is marginal for the 450K (350°F) exposure and test conditions.

STPI/LaRC-2/Chromic Acid Anodize Surface Preparation

STPI/LaRC-2 adhesive produced slightly higher initial results of the three metal-to-metal bonding systems examined. The initial lap shear strengths were of structural quality; however, the strength loss upon exposure to elevated temperature could be of concern. Testing at 450K (350°F) and 505K (450°F) resulted in a lap shear strength of 27.5 MPa (3990 psi) (25% loss) and 17.4 MPa (2530 psi) (53% loss). No change in the percent cohesive failure was evident to definitely indicate that a viscoelastic mechanical response was taking place.

The STPI/LaRC-2 adhesive system exhibited no significant drop in lap shear strength as a result of exposure to long-term elevated temperatures. The mean shear values, as seen in Table 2.4.1.3, are fluctuating in a relatively narrow range.

The creep resistance of this adhesive system is good, as no creep was recorded after 3,000 hours of exposure to 450K (350°F). The results of a similar study at 505K (450°F) were suspect due to a malfunction of the exposure oven. Three specimens failed after 1650 hours when a thermostat control failure allowed temperatures to rise to approximately 560K (550°F) for one to two hours. This severe temperature and stress condition was at the glass transition temperature of the resin and would, therefore, be expected to cause creep failure.

The effects of 322K(120°F)/95% R.H. exposure are not obvious. Ambient testing of 1,000 hour humidity exposure specimens resulted in no significant change in shear strength. Elevated temperature testing (i.e., 450K (350°F)) of 1,000 hour exposure specimens resulted in a 29% decrease in strength. This combined hot/wet exposure and subsequent elevated temperature testing does not reduce performance to the point that structural integrity is lost.

Skydrol exposure has a minor influence on the durability on STPI/LaRC-2 stressed lap shear strengths. After 1,000 hours exposure to Skydrol at 25% of ultimate strength,

testing at ambient temperature resulted in 32.2 MPa (4670 psi) (12% strength loss). Testing of similarily exposed specimens at 450K (350°F) produced shear strengths of 24.5 MPa (3550 psi) (11% strength loss). STPI/LaRC-2 maintained excellent structural integrity at both test conditions.

PAE SO_2/Chromic Acid Anodize Surface Preparation

PAE SO_2 typically resulted in the lowest mean shear strength values (see Figures 2.4.1.1 and 2.4.1.2) of the adhesive systems tested. Performance was however, above the design requirements for structural adhesives. The relative strength loss with exposure was consistent with other polymer systems. Initial exposure to elevated temperatures of 450K (350°F) and 505K (450°F) resulted in a lap shear strength of 21.2 MPa (3070 psi) (9% decrease) and 16.8 MPa (2440 psi) (28% decrease), respectively. As the test temperature is increased there appears to be some thermoplastic yielding, resulting in lower shear values and increased percentages of cohesive failures.

PAE-SO_2 test specimens exposed to elevated temperatures (450K (350°F) and 505K (450°F)) have shown very good resistance to creep. No creep was recorded after 3,000 hours of exposure to these temperatures.

Exposure to humidity appears to have a significant effect upon lap shear strength of PAE SO_2. One thousand hours of exposure resulted in lap shear strengths of 15.3 MPa (2220 psi) (34% decrease), and 14.5 MPa (2110 psi) (32% decrease), for ambient and 450K (350°F), respectively. All lap shear specimens failure modes were primarily cohesive after humidity exposure. The resulting strengths after exposure are very near the lower limit for structural adhesives.

Skydrol exposure significantly degrades lap shear strength. Specimens stressed to 25% of ultimate strength and exposed to Skydrol failed in 625 hours, or less. These failed specimens also exhibited a low percentage of cohesive failure.

2.4.2 Crack Extension Test and Analysis

The crack extension test is a method for assessing the effects of stress upon an adhesive bond system. It is discriminating in determining variation in adherend surface preparation parameters and adhesive environmental durability. The extending

crack tip will propagate through the path of least resistance. Therefore, it will locate the weakest phase of an adhesive joint system.

The tests were conducted at ambient temperature, 450K (350°F), and 505K (450°F). Additional crack extension tests were performed with humidity exposure at 322K (120°F)/95% R.H., and long-term aging at 450K (350°F) and 505K (450°F).

A summary of crack extension results for PPQ (both 10 volt CAA and Pasa-Jell 107), STPI/LaRC-2, and PAE SO_2 are presented in Figures 2.4.2.1 through 2.4.2.4. This information is also presented in Tables 2.4.1.1 through 2.4.1.4. Individual specimen data is also presented in the Appendix.

PPQ/Chromic Acid Anodize and Pasa-Jell 107 Surface Preparations

Since the crack extension test is a good measure of the quality of surface preparation, a direct comparison may be made between the chromic acid anodize and Pasa-Jell 107 treatments used with the PPQ adhesive.

In general, there did not appear to be a significant difference in the resistance to crack growth of PPQ on 10 volt CAA or Pasa-Jell 107 at elevated temperatures (450K (350°F) and 505K (450°F)). The results of 3,000 hours of exposure are in Figures 2.4.2.1 and 2.4.2.2. The initial crack growth for the CAA and Pasa-Jell systems at 450K (350°F) were 21.6 mm (0.85 inches) and 21.1 mm (0.83 inches), respectively. During the course of exposure, crack growths remained within 1.3 mm (0.05 inches) range. A significant change in crack growth between surface preparations did occur after 3,000 hours of exposure to 505K (450°F). Between 2,000 and 3,000 hours the mean crack length for the CAA test specimens increased by 4.5 mm (0.18 inches) while the Pasa-Jell specimens remained unchanged. This increase for the CAA is attributable to two specimens of the test group. Removing those specimens from the sample group would result in similar mean extensions between 450K (350°F) and 505K (450°F). Figures 2.4.2.1 and 2.4.2.2 illustrate the relative mean increase in crack length after 3,000 hours exposure to the given environment.

FIGURE 2.4.2.1
PPQ CRACK GROWTH AS A FUNCTION OF ENVIRONMENTAL EXPOSURE
ADHEREND: 6AL-4V TITANIUM
SURFACE PREP: 10 VOLT CAA

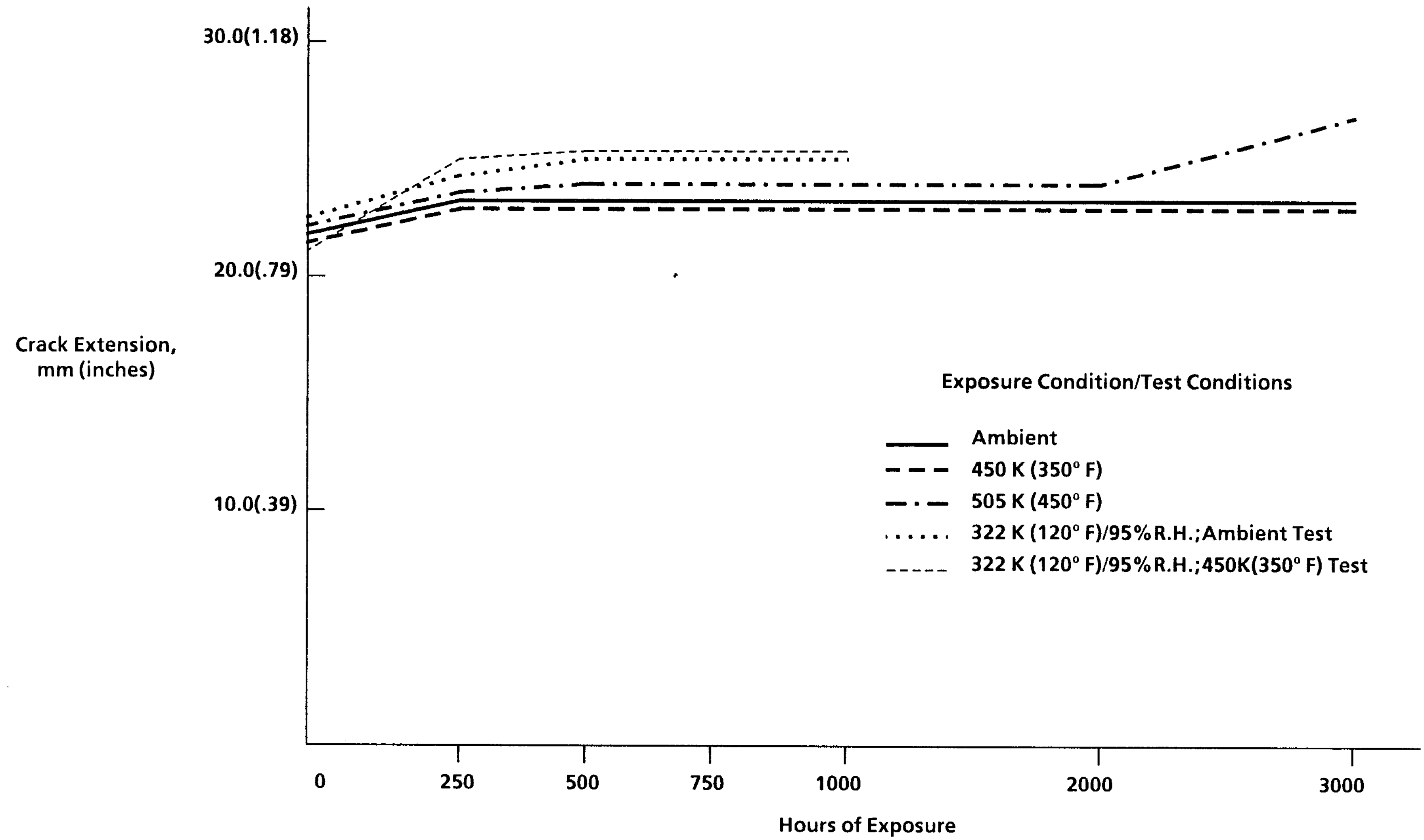


FIGURE 2.4.2.2
PPQ CRACK GROWTH AS A FUNCTION OF ENVIRONMENTAL EXPOSURE
ADHEREND: 6AL-4V TITANIUM
SURFACE PREP: PASA-JELL 107

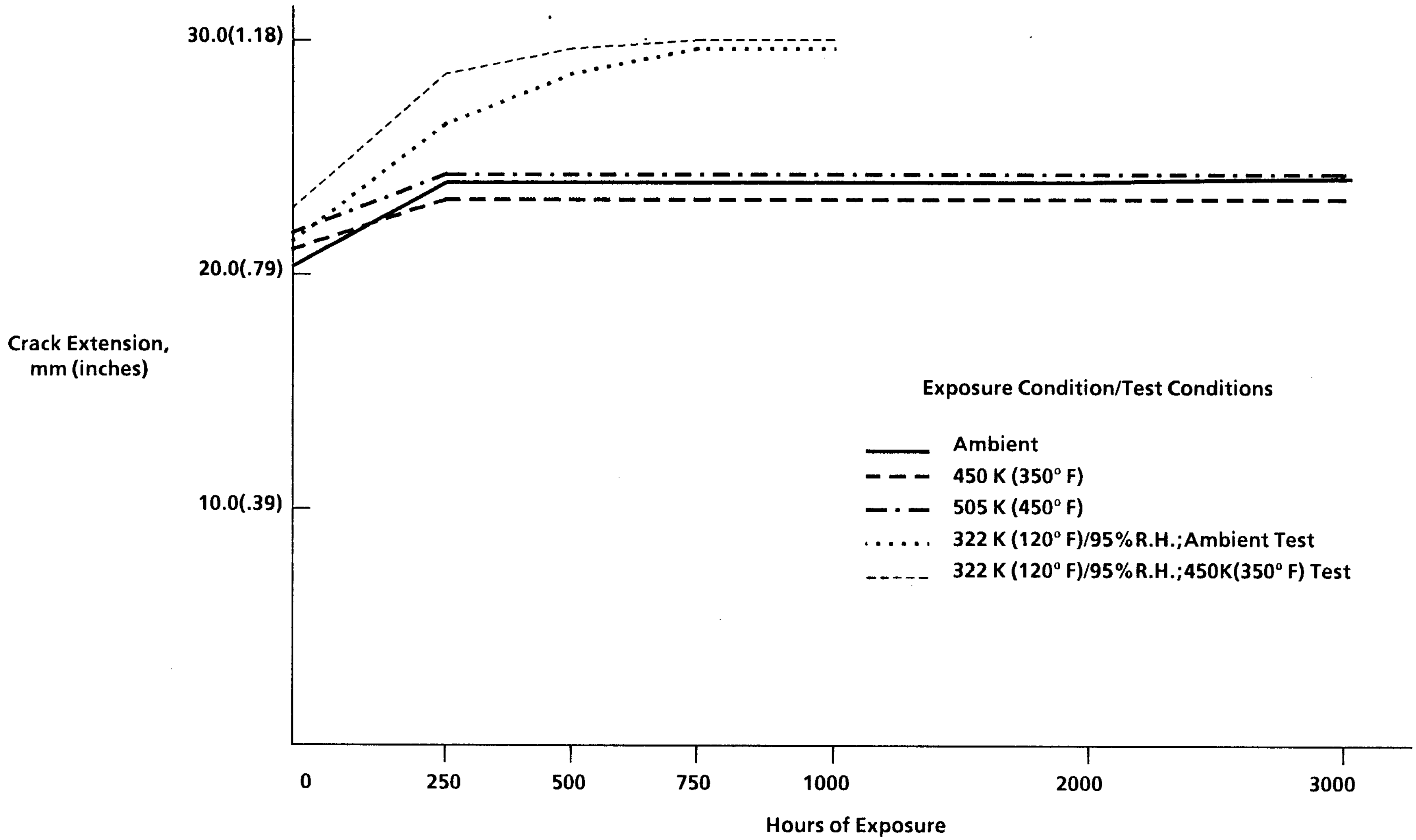


FIGURE 2.4.2.3
STPI/LaRC-2 CRACK GROWTH AS A FUNCTION OF ENVIRONMENTAL EXPOSURE
ADHEREND: 6AL-4V TITANIUM
SURFACE PREP: 10 VOLT CAA

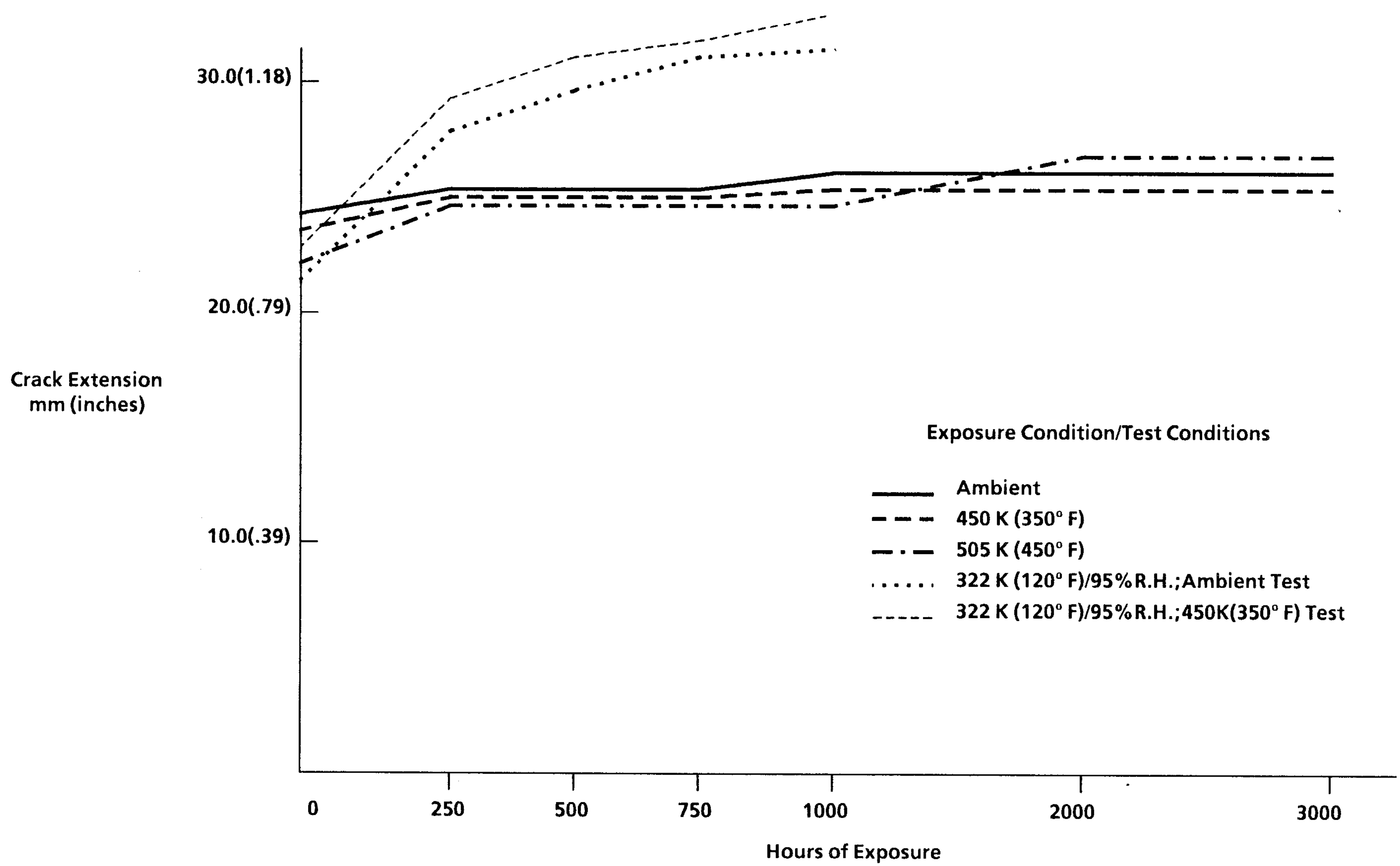


FIGURE 2.4.2.4
PAE SO_2 CRACK GROWTH AS A FUNCTION OF ENVIRONMENTAL EXPOSURE
ADHEREND: 6AL-4V TITANIUM
SURFACE PREP: 10 VOLT CAA

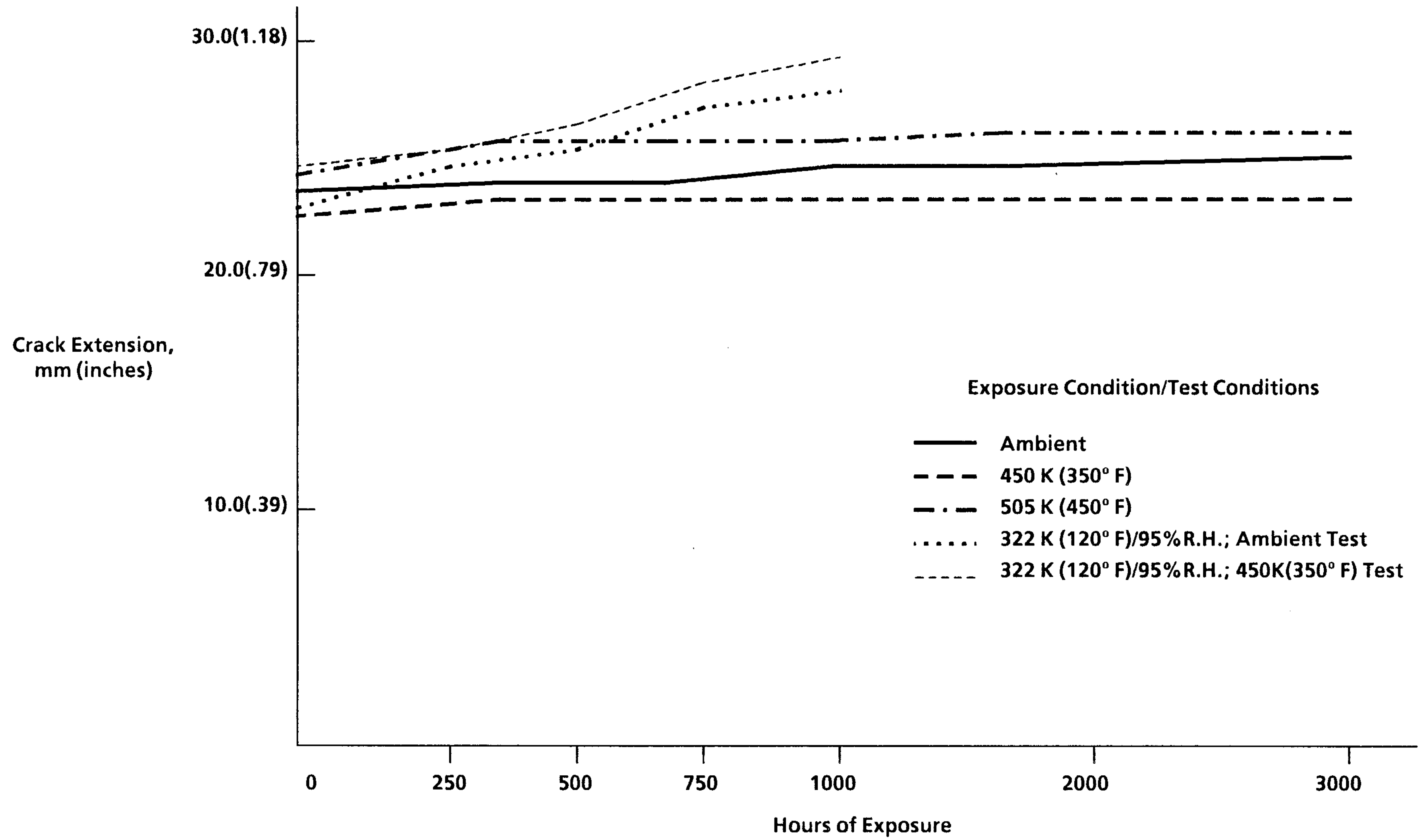


Table 2.4.2.1

CRACK EXTENSION AS A FUNCTION OF 3000 HOUR TEMPERATURE EXPOSURE

Adhesive System	Exposure Conditions	Increase in Crack Length	Percent Increase in Crack Length
PPQ/CAA	Ambient Temp	2.0 mm (0.08 inch)	10%
	450K (350°F)	2.0 mm (0.08 inch)	9%
	505K (450°F)	6.6 mm (0.26 inch)	30%
PPQ/Pasa-Jell	Ambient Temp.	3.3 mm (0.13 inch)	16%
	450K (350°F)	1.5 mm (0.06 inch)	7%
	505K (450°F)	1.8 mm (0.07 inch)	8%

These specimens are still in exposure and the mode of failure, i.e., cohesive, adhesive, adhesive/primer interface, primer/oxide interface, etc.) was not determined.

Humidity exposure for 1,000 hours produced consistently greater crack growth than high temperature exposures for the same period of time. At the completion of exposure, samples were opened for determination of failure mode. One hundred percent cohesive failure was observed on both surface preparations. It would appear that a stressed, exposed adhesive is sensitive to a hot/humid environment, and that the weakest portion of the bond system is within the adhesive and not in the adherend surface preparation.

Table 2.4.2.2

CRACK EXTENSION AS A FUNCTION OF 1000 HOUR HUMIDITY EXPOSURE

Adhesive System	Exposure Conditions	Increase in Crack Length	Percent Increase in Crack Length
PPQ/CAA	Ambient Temp	4.0 mm (0.16 inch)	19%
	450K (350°F)	3.8 mm (0.15 inch)	18%
PPQ/Pasa-Jell	Ambient Temp.	6.6 mm (0.26 inch)	31%
	450K (350°F)	7.1 mm (0.28 inch)	34%

STPI/LaRC-2/Chromic Acid Anodize Surface Preparation

During exposure to elevated temperature in air, STPI/LaRC-2 performed well. After 3,000 hours exposure to elevated temperatures, the magnitude of the crack growth and the percent of crack extension was considerably less than it was for the 1000 hour humidity specimens (Tables 2.4.2.3 and 2.4.2.4).

Table 2.4.2.3

CRACK EXTENSION AS A FUNCTION OF 3000 HOUR TEMPERATURE EXPOSURE

Adhesive System	Exposure Conditions	Increase in Crack Length	Percent Increase in Crack Length
STPI/LaRC-2	Ambient Temp	2.0 mm (0.08 inch)	8%
	450K (350°F)	2.5 mm (0.10 inch)	10%
	505K (450°F)	4.8 mm (0.19 inch)	21%

Table 2.4.2.4

CRACK EXTENSION AS A FUNCTION OF 1000 HOUR HUMIDITY EXPOSURE

Adhesive System	Exposure Conditions	Increase in Crack Length	Percent Increase in Crack Length
STPI/LaRC-2	Ambient Temp	9.2 mm (0.36 inch)	42%
	450K (350°F)	9.9 mm (0.39 inch)	43%

The failed humidity exposure specimens exhibited 40-50% cohesive failures. It would appear that the exposed advancing crack tip within the adhesive is sensitive to a 322K (120°F)/95% R.H. environment.

PAE SO_2/Chromic Acid Anodize Surface Preparation

The resistance to crack growth of PAE SO_2 in elevated temperature environments is very good. The magnitude of crack extension and percent increase from the initial condition exhibit no significant change after 3,000 hours exposure (Table 2.4.2.5).

Table 2.4.2.5

CRACK EXTENSION AS A FUNCTION OF 3000 HOUR TEMPERATURE EXPOSURE

Adhesive System	Exposure Conditions	Increase in Crack Length	Percent Increase in Crack Length
PAE SO_2	Ambient Temp	2.0 mm (0.08 inch)	8%
	450K (350°F)	1.0 mm (0.04 inch)	10%
	505K (450°F)	2.3 mm (0.09 inch)	10%

Similar to the other adhesives tested, PAE-SO_2 crack growth increased significantly during humidity exposure (Table 2.4.2.6). After the completion of environmental exposure, the test specimens exhibited 100% cohesive failures.

Table 2.4.2.6

CRACK EXTENSION AS A FUNCTION OF 1000 HOUR HUMIDITY EXPOSURE

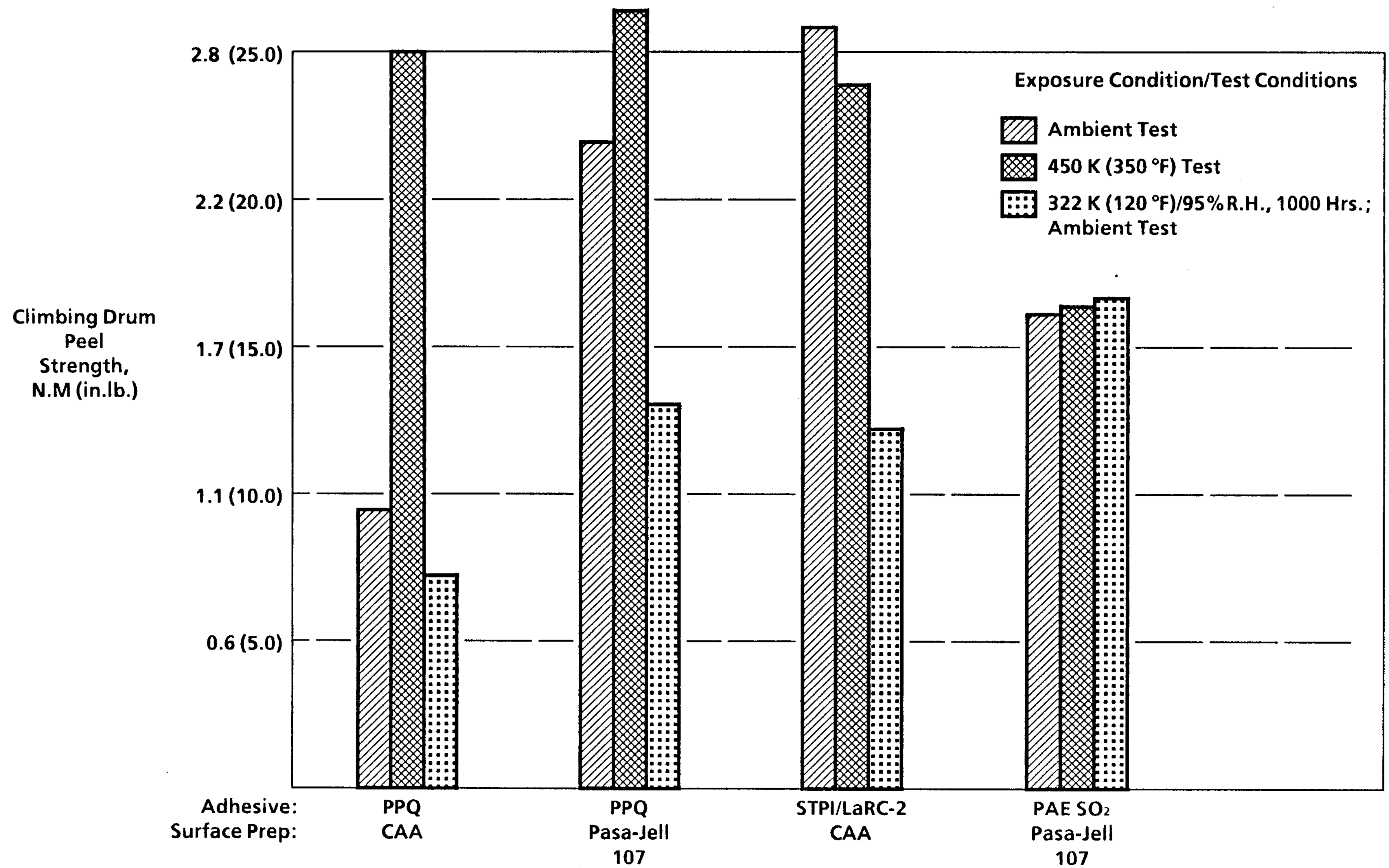
Adhesive System	Exposure Conditions	Increase in Crack Length	Percent Increase in Crack Length
PAE SO_2	Ambient Temp	5.0 mm (0.20 inch)	21%
	450K (350°F)	5.3 mm (0.21 inch)	22%

2.4.3 Climbing Drum Peel Test and Analysis

The climbing drum peel test is a good indication of the toughness properties of the adhesives tested. Peel strength was recorded at ambient temperature, 450K (350°F), and after 1,000 hours of exposure to 322K (120°F)/95% relative humidity.

A summary of climbing drum peel strength values for PPQ, STPI/LaRC-2, and PAE SO_2 are presented in tabular form in Tables 2.4.1.1 through 2.4.1.4. This information is also presented graphically in Figure 2.4.3.1. Individual data points are presented in the Appendix.

FIGURE 2.4.3.1
CLIMBING DRUM PEEL STRENGTH OF EXPERIMENTAL POLYMERS
ADHEREND: 6AL-4V TITANIUM



Peel performance of PPQ on 10 volt CAA and Pasa-Jell 107 treated titanium was examined to determine the relative quality of the two methods of surface preparation. The peel strength, at ambient test temperatures, was significantly greater for Pasa-Jell 107 than 10 volt CAA. Pasa-Jell produced 2.5 N.M. (22.0 in.lb.) with 85% cohesive failure while the CAA specimens had peel strengths of 1.1 N.M. (9.5 in.lb), failures occurring between the adhesive and the primer. The environmentally exposed specimens exhibited no significant differences between CAA and Pasa-Jell 107. Both exhibited primarily adhesive failures after humidity exposure and primarily cohesive failures after 450K (350°F) exposure.

Climbing drum peel strengths of the STPI/LaRC-2 adhesive were relatively high (3.0 N.M. (26.6 in.lb) at ambient and 2.7 N.M. (24.1 in.lb) at 450K (350°F) test temperatures. Failure modes of these test specimens were primarily cohesive (75%). However, peel strengths decreased to 1.4 N.M. (12.2 in.lb) after 1000 hour humidity exposure, with the failure mode changing to 75% adhesive.

The PAE SO_2 adhesive exhibited very consistent peel properties, averaging 1.8 N.M. (16 in.lb) to 1.9 N.M. (17 in.lb), at all test conditions. The failure modes were 100% cohesive, indicating the excellent toughness of this polymer.

2.4.4 Metal-to-Metal Bonding of Stainless Steel

Supplementary studies were conducted on the ability of the experimental polymers to form large area structural bonds with sulfuric acid anodized (SAA) 17-7 PH stainless steel. Stainless steel panels (0.09 m^2 (1 ft^2)) were adhesively bonded with adhesive films prepared from each experimental polymer. Ultrasonic scans of the bonded stainless steel panels indicated that the panels were good quality but some voids were identified. Panels were then machined into notched single lap shear specimens. Shear strengths were determined at ambient temperature, 450K (350°F) and 505K (450°F); with additional testing after exposure to 322K (120°F)/95% R.H. A summary of this data is available in Figure 2.4.4.1, in tabular form in Table 2.4.4.1, and individual specimen data is in the Appendix.

FIGURE 2.4.4.1
LAP SHEAR STRENGTH OF EXPERIMENTAL POLYMERS
ADHEREND: 17-7 PH STAINLESS STEEL
SURFACE PREP: 2 VOLT SULFURIC ACID ANODIZE

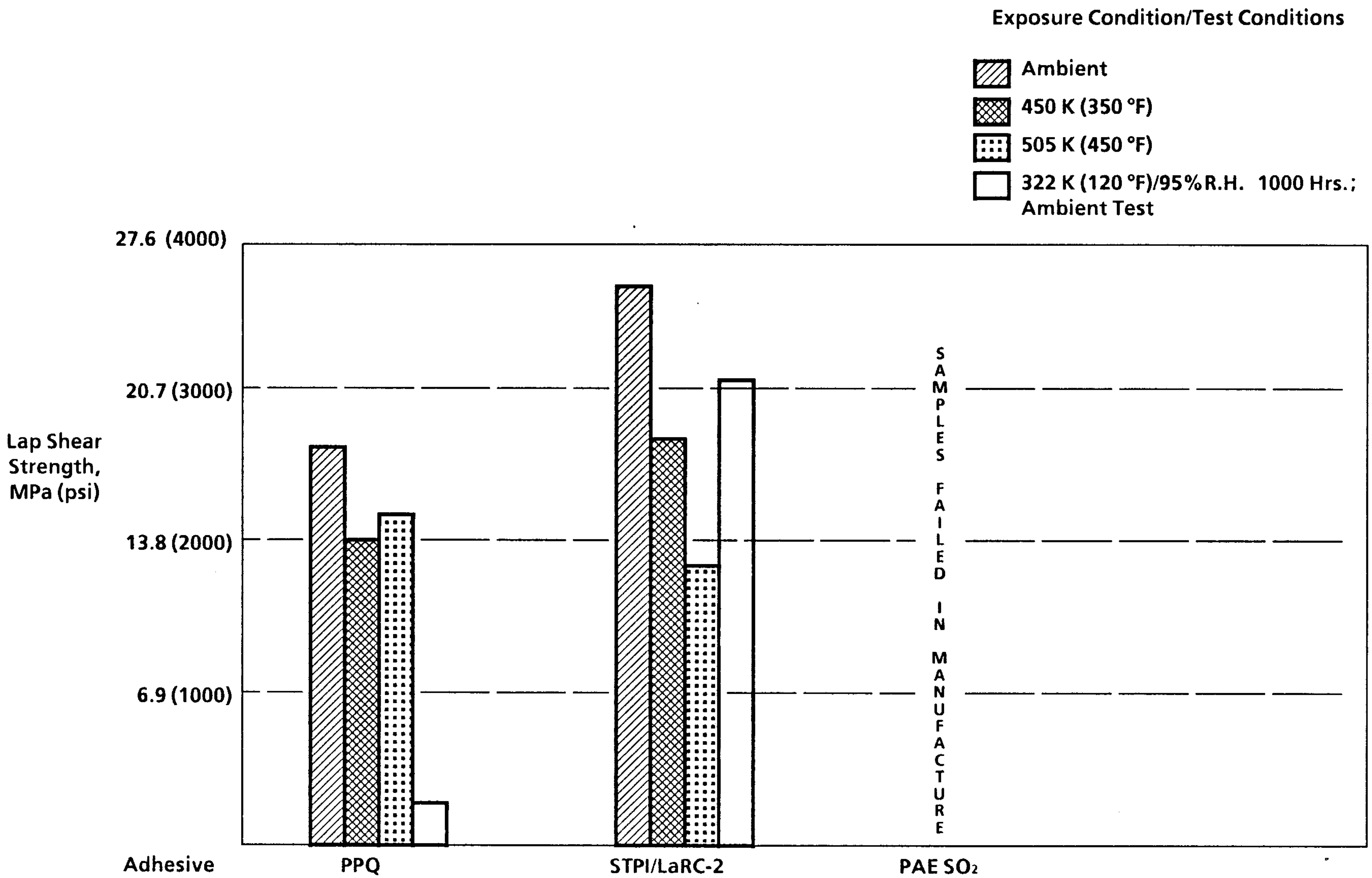


TABLE 2.4.4.1

LAP SHEAR STRENGTH OF EXPERIMENTAL POLYMERS

ADHEREND - 17-7 PH STAINLESS STEEL
SURFACE PREPARATION - SULFURIC ACID ANODIZE

TEST CONDITION	PPQ MPa (psi)	STPI/LaRC-2 MPa (psi)	PAE SO_2 MPa (psi)
Ambient, Initial	18.0 (2610)	25.4 (3690)	*
450K (350°F), Initial	13.9 (2010)	17.9 (2600)	*
505K (450°F), Initial	15.0 (2170)	12.8 (1850)	*
Ambient After Exposure to 322K (120°F)/90% R.H.	1.7 (250)	21.2 (3070)	*

* Samples failed while being machined into lap shear specimens.

The test results obtained in this study were similar to those of the titanium lap shear study. However, the values for stainless steel were consistently lower than those for titanium which may reflect the inability of these polymers to form good large area bonds. The drop in shear strengths associated with increased temperature does not appear to be attributable to yielding of the adhesive due to loading. Rather, a poor bond exists between the primer and the SAA substrate, as indicated by the low percentage of cohesive failure.

Additional work must be conducted to optimize the SAA process for 17-7 PH stainless steel.

2.5 Preparation of LaRC-TPI Honeycomb Sandwich Test Specimens

The adherends used in this section were titanium for both face sheet and honeycomb core. The planned test matrix as shown in Table 2.5.1 includes: flatwise tension, edgewise compression, short beam shear and sandwich climbing drum peel specimens. The configuration of each specimen is shown in Figure 2.5.1. Surface preparation for the titanium adherends was chromic acid anodize (10 volt CAA) per Boeing Process Specification BAC 5890. All test specimens were prepared by cutting appropriate sized pieces of adhesive film, assembling the adherends and film, and vacuum bagging. All honeycomb sandwich test specimens were autoclave cured as follows:

TABLE 2.5.1

LaRC-TPI TEST MATRIX
HONEYCOMB SANDWICH TEST SPECIMENS *
ADHEREND - 6Al-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

Test Condition	FLATWISE TENSION MPa (psi)	EDGEWISE COMPRESSION MPa (psi)	SHORT BEAM SHEAR MPa (psi)	CLIMBING DRUM PEEL N.M. (in.lb)
Ambient Initial	4	4	4	4
219 K (-65°F) Initial	4	4	4	4
450 K (350°F) Initial	4	4	4	4
505 K (450°F) Initial	4	4	4	4
Ambient after exposure to 322 K (120°F)/95% RH 1000 hrs.	4	4	4	-
450 K (350°F) after exposure to 322 K (120°F) 95% RH 1000 hrs.	4	4	4	-
Ambient after unstressed exposure to Skydrol at ambient. 1000 hrs.	4	4	4	-
450 K (350°F) after unstressed exposure to Skydrol at ambient. 1000 hrs.	4	4	4	-
Ambient after exposure to Skydrol at ambient. 1000 hrs. (stressed at 25% of ultimate)	-	-	4	-
450 K (350°F) after exposure to Skydrol at ambient. 1000 hrs. (stressed at 25% of ultimate)	-	-	4	-
Ambient after exposure to 450 K (350°F) in air				
1000 hrs.	4	4	4	4
3000 hrs.	4	4	4	4
450 K (350°F) after exposure to 450 K (350°F) in air				
1000 hrs.	4	4	4	4
3000 hrs.	4	4	4	4
Ambient after exposure to 505 K (450°F) in air				
1000 hrs.	4	4	4	4
3000 hrs.	4	4	4	4
505 K (450°F) after exposure to 505 K (450°F) in air				
1000 hrs.	4	4	4	4
3000 hrs.	4	4	4	4

* Number of specimens each condition

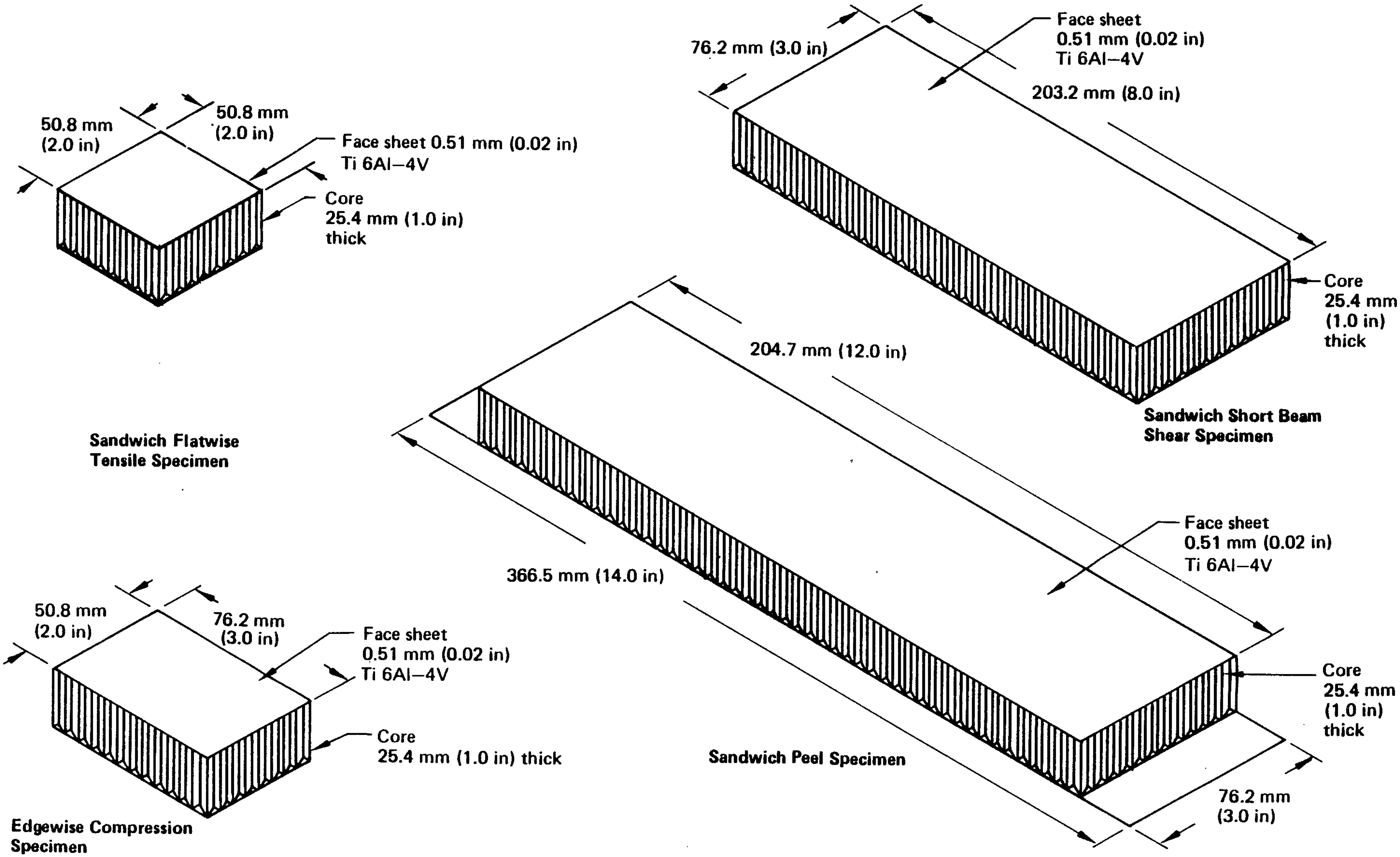


Figure 2.5.1 Honeycomb Sandwich Mechanical Test Specimens

- o LaRC-TPI
  1. Apply vacuum and .31 MPa (45 psi) autoclave pressure
  2. Heat to 616K (650°F) at 3K (5°F)/minute
  3. Hold at 616K (650°F) for 90 minutes
  4. Cool to below 338K (150°F) before releasing pressure

2.6 LaRC-TPI Honeycomb Bonding Resin Process Development

Preliminary screening of the commercially produced LaRC-TPI resin was completed on titanium lap shear and honeycomb sandwich flatwise tensile specimens. The minimum requirements for flatwise tensile strengths were 4.5 MPa (700 psi) at ambient, and 3.1 MPa (450 psi) at 505K (450°F) test temperatures.

Since the adhesive film did not (by itself) form an adequate honeycomb core to skin bond, primarily due to the low adhesive flow, a roller coated fillet was applied to the honeycomb surface. This fillet was prepared from LaRC-TPI resin with various loading levels of aluminum powder and Cabosil (fumed silica). Variations in fillet size, solvent type, application methods, and adhesive film preparation methods were all evaluated as methods to improve the honeycomb core to face sheet bond strength.

Initial honeycomb core bonding efforts concentrated on preparing a fillet material from the solvent solution (diglyme) of LaRC-TPI resin to improve the bond strength between the titanium core and face sheet. A paste was initially prepared from LaRC-TPI resin with aluminum powder (3M EC1101) and Cabosil (fumed silica). The filler loading levels were 20 phr (parts per hundred resin solids) for the aluminum powder and 10 phr for the Cabosil. Comparisons were also made with a roller coated commercial polyimide paste product (BR-35) from American Cyanamid. The filled LaRC-TPI resin was roller coated on LaRC-TPI primed chromic acid anodized titanium core (6.4 mm (0.25 inch) cell size, 25.4 mm (1.0 inch) thick). The fillet was oven dried in incremental 28K (50°F)/30 minute steps to 436K (325°F) to remove the residual solvent. Test specimens were assembled with a 2.5 mm (0.01 inch) thick LaRC-TPI supported adhesive film with volatile content of approximately 1.0 weight percent.

Additional LaRC-TPI fillet material was prepared with higher loading levels of the aluminum powder (25, 33, and 40 phr). Variations in the fillet size between 0.5 mm (0.02 inch) and 1.0 mm (0.04 inch) were also evaluated in efforts to improve the flatwise tensile properties. Aluminum powder loaded LaRC-TPI resin was also

prepared with 10 weight percent methanol solvent in order to improve processing ease and fillet formation. Test specimens were assembled as previously discussed.

Methods to improve the fabrication of the LaRC-TPI adhesive film were also evaluated to improve bond properties. Oven drying methods were modified to eliminate some problems encountered with solvent volatization and film bubbling. Thicker adhesive films 0.36 mm (0.014 inch) with a slightly higher volatile content (2% - 4%) were also fabricated to improve the ability of the adhesive film to form a fillet and provide better flow properties. Application of undiluted resin to both honeycomb core and adhesive film prior to test specimen fabrication was also evaluated as a method to improve bond properties.

2.7 LaRC-TPI Resin Honeycomb Bonding Test and Analysis

The initial fillet materials evaluated for honeycomb core bonding included: LaRC-TPI resin prepared with aluminum (20 phr) and Cabosil (10 phr), and BR-35 (American Cyanamid). Ambient flatwise tensile strengths of the bonded specimens ranged from 1.4 MPa (200 psi) to 2.1 MPa (300 psi) for all three fillet materials evaluated. Visual examination of the failed surfaces indicated that the aluminum filled LaRC-TPI formed a more coherent fillet when compared to the Cabosil filled material or BR-35. At this point, the decision was made to continue all filleting work with the aluminum powder.

Further evaluation of the aluminum filled LaRC-TPI resin was completed at loading levels of 25, 33, and 40 phr. The resulting flatwise tensile strengths were slightly improved from 2.1 MPa (310 psi) to 3.4 MPa (490 psi), as shown in Table 2.7.1. However, there was no correlation between fillet size/aluminum loading levels and the resulting flatwise tensile strength properties. Visual examination of the surfaces indicated that all specimens failed adhesively between the adhesive film and the roller coated core. Excessive bubbling for the 2.5 mm (0.010 inch) thick supported LaRC-TPI adhesive film were also noted.

TABLE 2.7.1

FLATWISE TENSILE PROPERTIES: LaRC-TPI FILM

FILLETING MATERIAL	FILLET SIZE mm (inch)		FLATWISE TENSILE STRENGTH MPa (psi)	
LaRC-TPI & 25 PHR Aluminum	0.5	(0.02)	3.4	(490)
	1.0	(0.04)	2.2	(320)
LaRC-TPI & 33 PHR Aluminum	0.5	(0.02)	2.9	(420)
	1.0	(0.04)	2.1	(310)
LaRC-TPI & 40 PHR Aluminum	0.5	(0.02)	2.3	(330)
	1.0	(0.04)	3.1	(450)

Efforts to improve the ability of aluminum filled LaRC-TPI resin to form fillets on honeycomb core by adding methanol solvent (10 weight percent) were somewhat successful. Processing ease and fillet formation were improved, but no observable differences in flatwise tensile strengths were noted.

The use of a thicker LaRC-TPI supported adhesive film in combination with a resin layer applied to both honeycomb core and adhesive film, improved ambient temperature flatwise tensile strengths from 3.2 MPa (420 psi) to 3.9 MPa (470 psi). The resin layer applied to both adhesive film and filleted core resulted in a failure dominated by the porous LaRC-TPI resin.

2.8 LaRC-TPI Honeycomb Bonding Powder Process Development

The objective of this work was to determine if the incorporation of LaRC-TPI powder into the honeycomb bond process would increase the flatwise tensile strength to the desired 4.5 MPa (700 psi) level at ambient temperature.

A 50 gram sample of LaRC-TPI powder produced by Mitsui Toatsu (lot 72-501) was received from NASA-Langley. The powder is a low molecular weight semi-crystalline polyimide which increases in molecular weight upon heating. Two approaches were evaluated. The first approach used hot melt and paste techniques to obtain LaRC-TPI fillets on titanium honeycomb core. The second approach prepared adhesive film by combining the LaRC-TPI powder with LaRC-TPI resin.

2.8.1 Powder Fillet Approach

The powder fillet approach for titanium core used the following procedures:

Hot Melt Technique

- o LaRC-TPI powder was heated to 533K (500°F) at 6K (10°F)/minute in contact with vapor degreased honeycomb core

- o LaRC-TPI powder was mixed with EC1101 aluminum powder (25 and 50 phr) then heated to 533K (500°F) at 6K (10°F)/minute in contact with CAA honeycomb core

- o Vapor degreased honeycomb core was heated to 700K (800°F) then immediately immersed in LaRC-TPI powder

- o A 0.5 mm (0.020 inch) casting of LaRC-TPI was fabricated at 505K (450°F), then vapor degreased honeycomb core was pressed into the casting and heated to 588K (600°F)

Paste Technique

- o LaRC-TPI powder was mixed with isopropyl alcohol (50 phr) to form a paste, then applied to the CAA honeycomb core as a fillet and heated to 533K (500°F)

- o LaRC-TPI powder was mixed with LaRC-TPI resin (lot 72-503) to form a paste, then applied to the CAA honeycomb core as a fillet and heated to 533K (500°F)

2.8.2 Powder/Resin Film Approach

The powder/resin approach used adhesive film formulated by combining LaRC-TPI powder and LaRC-TPI resin. The resin/powder solution was also applied to the core to aid fillet formation. Titanium honeycomb sandwich flatwise tensile specimens were fabricated to evaluate the bond strength.

LaRC-TPI powder (lot 72-501) was mixed with LaRC-TPI resin (lot 72-503) at a ratio of 100 grams resin to 25 grams of powder (75 phr). Style 112 fiberglass scrim with A1100 finish was stretched on a frame and primed with a dilute solution of the resin

(approximately 3 parts diglyme to 1 part supplied polymer solution). The LaRC-TPI resin/powder mixture was applied in single coats to both sides of the scrim to a total thickness of 0.3 mm (0.012 inch). The adhesive film was oven dried from 338K (150°F) to 477K (450°F) in increments of 28K (50°F)/30 minutes. The powder/resin mixture was roller coated onto chromic acid anodized, titanium honeycomb core samples, with 6.4 mm (0.25 inch) and 4.8 mm (0.19 inch) cell sizes. Two flatwise tensile specimens with chromic acid anodized 6Al-4V titanium face sheets were fabricated from each honeycomb core sample. The specimen configuration and cure are described in Section 2.5.

2.9 LaRC-TPI Powder Honeycomb Bonding Test and Analysis

2.9.1 Powder Fillet Test and Analysis

Efforts to hot-melt LaRC-TPI powder onto honeycomb core to form fillets were unsuccessful. The powder shrank away from the core upon heating. Similarly, the alcohol/powder paste technique did not form fillets because of the shrinkage when the alcohol evaporated. The paste made from powder plus resin formed fillets, but cracked during the oven drying at 477K (450°F).

2.9.2 Powder/Resin Film Test and Analysis

The results of the individual flatwise tensile specimens made from LaRC-TPI resin and powder (film and fillet) are shown below:

TABLE 2.9.2.1

FLATWISE TENSILE PROPERTIES: LaRC-TPI POWDER/RESIN FILM

	6.4 mm (0.25 inch) CELL SIZE	4.8 mm (0.19 inch) CELL SIZE
TEST	MPa (psi)	MPa (psi)
Ambient Flatwise Tensile	4.3 (630) 4.1 (590)	6.5 (940) 6.4 (920)

The modes of failure of the flatwise tensile specimens were mixed cohesive/adhesive to the core primer. The failure mode were similar for both core cell sizes tested.

These results clearly illustrate the increase in flatwise tensile strength that can be achieved using a smaller core cell size. Since flatwise tensile strength calculations are based on skin area rather than honeycomb core faying surface area, the core with the larger honeycomb area, namely the 4.8 mm (0.19 inch) cell size, should exhibit a higher calculated strength. For this test, a 56 percent increase in honeycomb area corresponded to about a 50 percent increase in calculated flatwise tensile strength.

For the same cell size core (6.4 mm (0.25 inch)), flatwise tensile strengths were improved by more than 0.7 M Pa (100 psi) by preparing adhesive film using powder in addition to the resin. Since this testing was limited by the amount of LaRC-TPI powder available, a process optimization study would be necessary to determine the maximum strength achievable using powder to enhance the honeycomb sandwich bond.

3.0 CONCLUSIONS AND RECOMMENDATIONS

3.1 Conclusions

- Polyphenylquinoxaline (PPQ) exhibited shear strengths of structural bond integrity in all test environments.

- Shear strength losses in PPQ, exposed to elevated temperatures, appear to be due to thermoplastic yielding of the adhesive at high loads. This would be attributed to the viscoelastic mechanical response expected to occur at temperatures approaching the glass transition temperature of the polymer.

- There does not appear to be a significant differences between the performance of chromic acid anodize or Pasa-Jell 107 treated titanium using PPQ adhesive. Any significant differences, observed in either crack extension or climbing drum peel, are explained by cohesive failure of the adhesive or adhesive failure between the adhesive/primer interface.

- Polyimide (STPI/LaRC-2) maintains shear strengths of structural bond quality in all test environments.

- Though STPI/LaRC-2 provided the highest ambient shear values of the study, its high temperature durability was poor. Strength losses of up to 53% from the ambient condition were observed after 3,000 hours exposure to 505K (450°F).

- Polyarylene ether (PAE SO_2) produced the lowest shear strengths but still maintained structural integrity in all test environment, except Skydrol.

- Humidity exposure appears to be the most influential factor in determining the crack extension behavior of all experimental polymers. Exposing the extending crack tip to this environment leads to accelerated degradation of the adhesive bond (as indicated by 100% cohesive failure of the adhesive).

- The bond strength of PPQ and STPI/LaRC-2 on sulfuric acid anodized stainless steel was very low; approaching non-structural quality. However, the SAA treatment used had not been optimized and could be a significant factor in the results.

- Polyarylene ether does not bond to 2 volt sulfuric acid anodized 17-7 PH stainless steel.

- The minimum flatwise tensile strength requirements for bonded titanium sandwich panels, 6.4 mm (0.25 inch) cell size, were not achieved using the LaRC-TPI film adhesive.

- The combination of LaRC-TPI resin/low molecular weight powder for both adhesive film and honeycomb core fillets is a promising approach to realizing the minimum strength requirements.

- Acceptable ambient sandwich flatwise tensile strengths were achieved by using 4.8 mm (0.19 inch) cell size honeycomb core in combination with the LaRC-TPI resin/powder approach.

3.2 Recommendations

- The PPQ and STPI/LaRC-2 polymers exhibited the greatest promise as metal-to-metal structural adhesives for high temperature applications. Trends in the environmental durability of these adhesives (i.e., viscoelastic response and some polymer degradation) were observed, but must be substantiated by similar testing over longer durations.

- Due to the poor bonding of sulfuric acid anodized stainless steel, further work should be conducted to optimize this process or find alternative techniques which will improve the high temperature performance of these adhesives with this adherend.

- The adhesive film prepared using a combination of LaRC-TPI powder and resin exhibited significant promise as a structural adhesive suitable for honeycomb sandwich bonding. Additional work to optimize this process is recommended.

4.0 REFERENCES

1. S. G. Hill, P. D. Peters, and C. L. Hendricks, "Evaluation of High Temperature Structural Adhesives for Extended Service - Phase I/II," NASA Contract Report 165944, July 1982.

2. S. G. Hill and C. L. Hendricks, "Evaluation of High Temperature Structural Adhesives for Extended Service - Phase III," NASA Contract Report 172163, July 1983.

3. C. L. Hendricks, S. G. Hill, and J. N. Hale, "Evaluation of High Temperature Structural Adhesives for Extended Service - Phase IV," NASA Contractor Report 177936, October 1985.

APPENDIX

SUMMARY OF INDIVIDUAL TEST VALUES

PPQ TEMPERATURE EXPOSURE INDIVIDUAL TEST VALUES
ADHEREND: 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

TEST	TEST TEMPERATURE		INITIAL		%C	EXPOSURE TIME 1000 HOURS		%C	3000 HOURS		%C
Lap Shear MPa (psi)	219K (-65°F)		32.2	(4670)	40						
			29.9	(5790)	75						
			38.1	(5520)	85						
			34.2	(4970)	95						
			40.7	(5900)	90						
		Avg.	37.0	(5370)							
	Ambient		36.9	(5350)	90						
			36.4	(5280)	100						
			35.5	(5150)	75						
			33.7	(4890)	75						
			32.8	(4750)	85						
		Avg.	35.0	(5080)							
	450K (350°F)		28.1	(4080)	100	26.3	(3810)	100	24.1	(3500)	100
			21.4	(3100)	90	26.6	(3850)	100	23.0	(3330)	100
			27.1	(3930)	100	26.6	(3850)	100	23.9	(3470)	100
			22.8	(3310)	90	27.4	(3970)	100	18.3	(2650)	100
			24.9	(3610)	90	27.0	(3910)	100	24.5	(3550)	100
		Avg.	24.9	(3610)		26.8	(3880)		22.8	(3300)	
	505K (450°F)		15.0	(2170)	60	22.8	(3300)	100	21.3	(3090)	100
			20.6	(2980)	100	21.7	(3150)	100	20.1	(2920)	100
			20.8	(3010)	100	22.4	(3250)	100	18.8	(2720)	75
			20.8	(3020)	100	21.0	(3050)	100	20.4	(2960)	100
			20.7	(3000)	100	18.6	(2690)	100	16.0	(2320)	60
		Avg.	19.6	(2840)		21.3	(3090)		19.3	(2800)	
Drum Peel N.M (in.lb)	Ambient		1.0	(9.0)	5						
			1.2	(11.0)	5						
			0.9	(8.0)	0						
			1.2	(9.5)	5						
		Avg.	1.1	(9.5)							
	450K (350°F)		2.4	(21.5)	30						
			3.1	(27.0)	95						
			2.7	(24.0)	90						
			3.2	(28.5)	95						
		Avg.	2.8	(25.0)							

%C - Percent Cohesive Failure

PPQ ENVIRONMENTAL EXPOSURE INDIVIDUAL RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

TEST	TEST TEMPERATURE		INITIAL NO EXPOSURE	%C	322K (120°F)/ 95% R.H. 1000 HOURS	%C	STRESSED SKYDROL AT AMBIENT # 1000 HOURS	%C
Lap Shear MPa (psi)	Ambient		36.9 (5350)	90	27.1 (3930)	90	33.4 (3550)	95
			36.4 (5280)	100	31.0 (4500)	100	35.9 (5200)	90
			35.5 (5150)	75	25.9 (3750)	100	28.6 (4150)	100
			33.7 (4890)	75	17.6 (2550)	90	24.1 (3500)	80
			32.8 (4750)	85	25.7 (3720)	85	34.6 (5020)	100
		Avg.	35.0 (5080)		25.4 (3690)		31.3 (4540)	
	450K (350°F)		28.1 (4080)	100	24.5 (3550)	100	12.6 (1820)	40
			21.4 (3100)	95	25.3 (3670)	100	20.8 (3020)	60
			27.1 (3930)	100	24.6 (3570)	100	21.8 (3160)	80
			22.8 (3310)	90	21.1 (3060)	100	19.2 (2780)	50
			24.9 (3610)	90	25.3 (3670)	100	21.5 (3120)	80
		Avg.	24.9 (3610)		24.1 (3500)		19.2 (2780)	
Drum Peel N.M (in.lb)	Ambient		1.0 (9.0)	5	0.8 (7.0)	0		
			1.2 (11.0)	5	0.7 (6.5)	0		
			0.9 (8.0)	0	0.6 (5.5)	0		
			1.2 (9.5)	5	0.9 (8.0)	0		
		Avg.	1.1 (9.5)		0.8 (7.0)			

%C - Percent Cohesive Failure

= Stressed at 25% of ultimate strength

PPQ CRACK EXTENSION INDIVIDUAL TEST RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

EXPOSURE		EXPOSURE TIME (HOURS) 0		500		1000		3000	
		mm	(inches)	mm	(inches)	mm	(inches)	mm	(inches)
Ambient		21.6	(0.85)	23.9	(0.94)	23.9	(0.94)	23.9	(0.94)
		23.1	(0.91)	24.9	(0.98)	24.9	(0.98)	25.1	(0.99)
		20.1	(0.79)	21.3	(0.84)	21.3	(0.84)	21.3	(0.84)
		21.1	(0.83)	22.9	(0.90)	23.1	(0.91)	23.1	(0.91)
	Average	21.3	(0.84)	23.4	(0.92)	23.4	(0.92)	23.4	(0.92)
450K (350°F)		22.6	(0.89)	23.4	(0.92)	24.1	(0.95)	24.1	(0.95)
		21.1	(0.83)	23.4	(0.92)	23.4	(0.92)	23.4	(0.92)
		21.3	(0.84)	22.6	(0.89)	23.1	(0.91)	23.1	(0.91)
		21.1	(0.83)	22.9	(0.90)	23.6	(0.93)	23.6	(0.93)
	Average	21.6	(0.85)	23.1	(0.91)	23.6	(0.93)	23.6	(0.93)
505K (450°F)		20.8	(0.82)	23.1	(0.82)	23.1	(0.91)	33.8	(1.33)
		22.4	(0.88)	23.9	(0.94)	24.6	(0.97)	25.4	(1.00)
		22.6	(0.89)	24.6	(0.97)	25.1	(0.99)	31.2	(1.23)
		21.3	(0.84)	23.1	(0.91)	23.1	(0.91)	23.1	(0.91)
	Average	21.8	(0.86)	23.6	(0.93)	23.9	(0.94)	28.4	(1.12)
322K (120°F)/		19.6	(0.77)	23.1	(0.91)	23.1	(0.91) 1/		
95% R.H.		21.8	(0.86)	26.2	(1.03)	26.2	(1.03)		
Tested at Ambient		20.8	(0.82)	24.9	(0.98)	25.4	(0.95)		
Temperature		20.3	(0.80)	23.4	(0.92)	24.1	(0.95)		
	Average	20.6	(0.81)	24.4	(0.96)	24.6	(0.97)		
322K (120°F)/		20.8	(0.82)	23.9	(0.94)	23.9	(0.94) 1/		
95% R.H.		20.8	(0.82)	25.1	(0.99)	26.2	(1.03)		
Tested after 450K		21.8	(0.86)	24.4	(0.96)	24.9	(0.98)		
(350°F)/10 min. Exp.		22.1	(0.84)	25.4	(1.00)	25.7	(1.01)		
	Average	21.3	(0.84)	24.6	(0.97)	25.1	(0.99)		

1/ All cohesive failures

PPQ TEMPERATURE EXPOSURE INDIVIDUAL TEST VALUES
ADHEREND: 6AL-4V TITANIUM
SURFACE PREPARATION - PASA-JELL

TEST	TEST TEMPERATURE		INITIAL		%C	EXPOSURE TIME 1000 HOURS		%C	3000 HOURS		%C
Lap Shear MPa (psi)	219K (-65°F)		37.1	(5380)	95						
			25.6	(3710)	80						
			30.0	(4350)	75						
			41.9	(6070)	100						
			40.3	(5840)	100						
		Avg.	35.0	(5070)							
	Ambient		22.7	(3290)	60						
			34.6	(5010)	100						
			34.8	(5050)	100						
			23.0	(3340)	75						
			34.1	(4950)	80						
		Avg.	29.9	(4330)							
	450K (350°F)		17.2	(2500)	60	23.2	(3360)	100	15.7	(2280)	100
			18.8	(2720	100	17.2	(2490)	70	24.2	(3510)	95
			19.1	(2770)	75	17.8	(2580)	90	24.0	(3480)	100
			17.5	(2540)	100	22.8	(3300)	100	25.2	(3660)	100
			18.2	(2640)	80	26.3	(3810)	100	24.5	(3550)	100
		Avg.	18.2	(2640)		21.4	(3110)		22.8	(3300)	
	505K (450°F)		20.4	(2960)	100	17.6	(2550)	85	17.4	(2520)	80
			16.9	(2450)	80	16.6	(2400)	80	13.5	(1960)	75
			16.6	(2400)	100	8.4	(1220)	60	17.7	(2560)	90
			17.9	(2600)	90	14.8	(2140)	90	12.5	(1810)	65
			20.8	(3010)	100	16.3	(2370)	90	16.0	(2320)	75
		Avg.	18.5	(2680)		14.8	(2140)		15.4	(2240)	
Drum Peel N.M (in.lb)	Ambient		2.2	(19.5)	60						
			2.5	(22.0)	100						
			2.8	(24.5)	90						
			2.5	(22.0)	85						
		Avg.	2.5	(22.0)							
	450K (350°F)		3.3	(29.5)	50						
			2.9	(25.5)	100						
			2.9	(26.0)	95						
			3.1	(27.0)	95						
		Avg.	3.1	(27.0)							

%C - Percent Cohesive Failure

PPQ ENVIRONMENTAL EXPOSURE INDIVIDUAL RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - PASA-JELL

TEST	TEST TEMPERATURE		INITIAL NO EXPOSURE	%C	322K (120°F)/ 95% R.H. 1000 HOURS	%C	STRESSED SKYDROL AT AMBIENT # 1000 HOURS	%C
Lap Shear MPa (psi)	Ambient		22.7 (3290)	60	22.8 (3300)	80	28.6 (4150)	60
			34.6 (5010)	100	17.9 (2600)	40	26.6 (3850)	80
			34.8 (5050)	100	21.0 (3050)	95	36.6 (5300)	100
			23.0 (3340)	75	27.9 (4050)	100	32.3 (4680)	100
			34.1 (4950)	80	24.5 (3550)	90	21.3 (3090)	80
		Avg.	29.9 (4330)		22.8 (3310)		29.0 (4210)	
	450K (350°F)		17.2 (2500)	60	20.4 (1960)	100	15.6 (2260)	90
			18.8 (2720)	100	18.8 (2730)	90	10.8 (1560)	60
			19.1 (2770)	75	16.1 (2340)	80	4.7 (680)	25 *
			17.5 (2540)	100	20.0 (2900)	100	16.5 (2390)	50
			18.2 (2640)	80	21.0 (3040)	100	15.0 (2180)	60
		Avg.	18.2 (2640)		19.2 (2790)		14.5 (2100)	
Drum Peel N.M (in.lb)	Ambient		2.2 (19.5)	60	2.2 (19.5)	30		
			2.5 (22.0)	100	1.2 (10.5)	25		
			2.8 (24.5)	90	1.2 (10.5)	5		
			2.5 (22.0)	85	1.4 (12.0)	60		
		Avg.	2.5 (22.0)		1.5 (13.0)			

%C - Percent Cohesive Failure

* Not included in shear strength average

- Stressed at 25% of ultimate strength

PPQ CRACK EXTENSION INDIVIDUAL TEST RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - PASA-JELL

EXPOSURE		EXPOSURE TIME (HOURS) 0		500		1000		3000	
		mm	(inches)	mm	(inches)	mm	(inches)	mm	(inches)
Ambient		20.8	(0.82)	22.6	(0.89)	22.9	(0.90)	23.6	(0.93)
		20.9	(0.81)	23.1	(0.91)	23.1	(0.91)	23.6	(0.93)
		19.8	(0.78)	23.4	(0.92)	23.4	(0.92)	23.6	(0.93)
		*		*		*		*	
	Average	20.3	(0.80)	23.1	(0.91)	23.1	(0.91)	23.6	(0.93)
450K (350°F)		21.3	(0.84)	22.1	(0.87)	22.6	(0.89)	22.6	(0.89)
		20.1	(0.79)	22.6	(0.89)	22.6	(0.89)	22.6	(0.89)
		21.3	(0.84)	23.1	(0.91)	23.1	(0.91)	23.1	(0.91)
		21.6	(0.85)	22.1	(0.87)	22.1	(0.87)	22.1	(0.87)
	Average	21.1	(0.83)	22.6	(0.89)	22.6	(0.89)	22.6	(0.89)
505K (450°F)		20.1	(0.79)	21.8	(0.86)	21.8	(0.86)	21.8	(0.86)
		23.1	(0.91)	24.1	(0.95)	24.4	(0.96)	24.4	(0.96)
		21.1	(0.83)	23.1	(0.91)	23.4	(0.92)	23.4	(0.92)
		22.4	(0.88)	23.9	(0.94)	23.9	(0.94)	23.9	(0.94)
	Average	21.6	(0.85)	23.4	(0.92)	23.4	(0.92)	23.4	(0.92)
322K (120°F)/		21.3	(0.84)	26.9	(1.06)	27.9	(1.10) 1/		
95% R.H.		21.1	(0.83)	27.4	(1.08)	28.2	(1.11)		
Tested at Ambient		20.8	(0.82)	25.4	(1.00)	25.9	(1.02)		
Temperature		22.1	(0.87)	26.7	(1.05)	29.2	(1.15)		
	Average	21.3	(0.84)	26.7	(1.05)	27.9	(1.10)		
322K (120°F)/		20.6	(0.81)	27.4	(1.08)	27.4	(1.08) 1/		
95% R.H.		20.6	(0.81)	26.7	(1.05)	26.9	(1.06)		
Tested After 450K		20.3	(0.80)	29.0	(1.14)	29.5	(1.16)		
(350°F)/10 Min. Exp.		21.3	(0.84)	27.7	(1.09)	27.7	(1.09)		
	Average	20.8	(0.82)	27.7	(1.09)	27.9	(1.10)		

* Specimen failed during machining

1/ All cohesive failures

STPI/LaRC-2 TEMPERATURE EXPOSURE INDIVIDUAL TEST VALUES
ADHEREND: 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

TEST	TEST TEMPERATURE		INITIAL		%C	EXPOSURE TIME 1000 HOURS		%C	3000 HOURS		%C
Lap Shear MPa (psi)	219K (-65°F)		37.0	(5370)	95						
			32.8	(4750)	75						
			38.1	(5530)	90						
			32.8	(4760)	60						
			36.0	(5220)	50						
		Avg.	35.4	(5130)							
	Ambient		32.8	(4750)	75						
			37.9	(5500)	85						
			38.3	(5550)	90						
			36.6	(5300)	90						
			38.6	(5590)	90						
		Avg.	36.8	(5340)							
	450K (350°F)		28.7	(4160)	90	25.9	(3750)	75	16.1	(2340)	45
			28.5	(4130)	90	23.6	(3420)	50	31.6	(4580)	90
			27.6	(4000)	95	23.0	(3340)	50	22.6	(3280)	70
			26.9	(3900)	85	27.9	(4040)	80	25.4	(3680)	85
			25.9	(3750)	80	19.9	(2890)	65	30.6	(4430)	80
		Avg.	27.5	(3990)		24.1	(3490)		25.3	(3660)	
	505K (450°F)		15.9	(2300)	90	22.8	(3300)	75	14.5	(2100)	70
			18.4	(2670)	80	17.4	(2520)	60	14.5	(2100)	75
			19.3	(2800)	75	19.6	(2840)	90	18.1	(2620)	70
			19.6	(2840)	90	21.4	(3100)	80	22.8	(3310)	100
			14.2	(2060)	80	15.3	(2220)	40	13.1	(1900)	65
		Avg.	17.4	(2530)		19.3	(2800)		16.6	(2410)	
Drum Peel N.M (in.lb)	Ambient		3.2	(28.1)	50						
			2.6	(23.1)	50						
			3.5	(30.6)	100						
			2.8	(24.4)	60						
		Avg.	3.0	(26.6)							
	450K (350°F)		1.9	(17.2)	25						
			2.9	(26.0)	80						
			2.9	(26.0)	95						
			3.1	(27.2)	80						
		Avg.	2.7	(24.1)							

%C - Percent Cohesive Failure

STPI/LaRC-2 ENVIRONMENTAL EXPOSURE INDIVIDUAL RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

TEST	TEST TEMPERATURE		INITIAL NO EXPOSURE		%C	322K (120°F)/ 95% R.H. 1000 HOURS		%C	STRESSED SKYDROL AT AMBIENT # 1000 HOURS		%C
Lap Shear	Ambient		32.8	(4750)	75	33.7	(4890)	80	30.6	(4430)	50
			37.9	(5500)	85	31.7	(4600)	60	36.2	(5250)	90
			38.3	(5550)	90	38.6	(5600)	80	25.9	(3750)	75
			36.6	(5300)	90	34.5	(5000)	75	32.4	(4700)	70
			38.6	(5340)	90	36.8	(5340)	90	35.9	(5200)	60
		Avg.	36.8	(5340)		35.1	(5090)		32.2	(4670)	
	450K (350°F)		28.7	(4160)	100	23.4	(3400)	70	25.2	(3650)	80
			28.5	(4130)	90	21.4	(3100)	75	25.2	(3650)	95
			27.6	(4000)	95	20.7	(3000)	90	25.5	(3700)	60
			26.9	(3900)	85	18.6	(2690)	75	24.1	(3500)	75
			25.9	(3750)	80	13.0	(1890)	50	22.5	(3260)	65
		Avg.	27.5	(3990)		19.4	(2820)		24.5	(3550)	
Drum Peel N.M (in.lb)	Ambient		3.2	(28.1)	50	1.0	(8.8)	40			
			2.6	(23.1)	50	1.9	(16.3)	20			
			3.5	(30.6)	100	1.3	(11.3)	10			
			2.8	(24.4)	60	1.4	(12.5)	5			
		Avg.	3.0	(26.6)		1.4	(12.2)				

%C - Percent Cohesive Failure

- Stressed at 25% of ultimate strength

STPI/LaRC-2 CRACK EXTENSION INDIVIDUAL TEST RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

EXPOSURE		EXPOSURE TIME (HOURS) 0		500		1000		3000	
		mm	(inches)	mm	(inches)	mm	(inches)	mm	(inches)
Ambient		26.9	(1.06)	27.7	(1.09)	29.2	(1.15)	30.0	(1.18)
		28.4	(1.12)	29.2	(1.15)	29.2	(1.15)	29.2	(1.15)
		23.9	(0.94)	25.9	(1.02)	25.9	(1.02)	25.9	(1.02)
		20.6	(0.81)	22.1	(0.87)	22.4	(0.88)	22.6	(0.98)
	Avg.	25.0	(0.98)	26.2	(1.03)	26.7	(1.05)	26.9	(1.06)
450K (350°F)		26.4	(1.04)	29.5	(1.16)	29.5	(1.16)	29.5	(1.16)
		26.9	(1.06)	30.2	(1.19)	30.2	(1.19)	30.2	(1.19)
		20.6	(0.81)	21.6	(0.85)	21.6	(0.85)	21.8	(0.86)
		21.8	(0.86)	23.4	(0.92)	24.4	(0.96)	24.4	(0.96)
	Avg.	23.9	(0.94)	26.2	(1.03)	26.4	(1.04)	26.4	(1.04)
505K (450°F)		21.1	(0.83)	23.9	(0.94)	25.1	(0.99)	26.9	(1.06)
		26.2	(1.03)	29.2	(1.15)	29.2	(1.15)	29.7	(1.17)
		21.3	(0.84)	24.9	(0.98)	24.9	(0.98)	26.2	(1.03)
		21.3	(0.84)	24.9	(0.98)	24.9	(0.98)	27.2	(1.07)
	Avg.	22.6	(0.89)	25.7	(1.01)	25.9	(1.02)	27.4	(1.08)
322K (120°F)/		23.6	(0.93)	31.0	(1.22)	31.0	(1.22) 1/	—	
95% R.H. Tested		22.4	(0.88)	31.5	(1.24)	33.3	(1.31)	—	
at Ambient		20.6	(0.81)	25.7	(1.01)	25.7	(1.01)	—	
Temperature		20.8	(0.82)	29.5	(1.16)	33.5	(1.32)	—	
	Avg.	21.8	(0.86)	29.5	(1.16)	31.0	(1.22)		
322K(120°F)/		25.7	(1.01)	32.5	(1.28)	36.6	(1.44) 1/	—	
95% R.H. Tested		22.4	(0.88)	31.8	(1.25)	33.01	(1.30)	—	
After 450K (350°F)		23.6	(0.93)	32.0	(1.26)	35.3	(1.39)	—	
10 Min. Exposure		20.8	(0.82)	25.1	(0.99)	27.2	(1.07)	—	
	Avg.	23.1	(0.91)	30.5	(1.20)	33.0	(1.30)		

1/ 40% - 50% cohesive failures

PAE SO_2 TEMPERATURE EXPOSURE INDIVIDUAL TEST VALUES
ADHEREND: 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

TEST	TEST TEMPERATURE	INITIAL		%C	EXPOSURE TIME 1000 HOURS		%C	3000 HOURS		%C
Lap Shear MPa (psi)	219K (-65°F)	26.9	(3900)	20						
		25.7	(3730)	30						
		24.3	(3520)	30						
		23.1	(3350)	10						
		9.7	(1400)	15 *						
	Avg.	25.0	(3620)							
	Ambient	26.7	(3870)	75						
		22.1	(3200)	50						
		21.4	(3098)	60						
		26.3	(3810)	80						
		20.0	(2900)	40						
	Avg.	23.3	(2880)							
	450K (350°F)	23.1	(3350)	100	21.7	(3140)	85	22.6	(3280)	100
		21.8	(3160)	80	23.7	(3430)	95	20.8	(3020)	90
		18.6	(2700)	95	23.9	(3460)	90	19.2	(2790)	80
		23.8	(3450)	100	21.0	(3050)	90	20.4	(2960)	95
		18.6	(2700)	90	20.4	(2960)	80	20.6	(2990)	100
	Avg.	21.2	(3070)		22.1	(3210)		20.8	(3010)	
	505K (450°F)	16.9	(2450)	100	17.1	(2480)	85	17.0	(2460)	90
		19.3	(2800)	95	17.7	(2560)	80	12.1	(1760)	100
		14.6	(2120)	95	18.8	(2720)	90	19.3	(2800)	100
		13.8	(2000)	95	18.5	(2680)	95	15.9	(2800)	85
		19.6	(2840)	100	17.3	(2510)	90	15.7	(2280)	100
	Avg.	16.8	(2440)		17.9	(2590)		16.0	(2320)	
Drum Peel N.M. (in.lb.)	Ambient	2.0	(17.5)	100						
		2.0	(17.5)	100						
		1.6	(13.8)	100						
		1.8	(16.3)	100						
	Avg.	1.8	(16.3)							
	450K (350°F)	1.8	(15.6)	95						
		1.8	(16.3)	100						
		1.8	(15.6)	100						
		1.9	(16.9)	100						
	Avg.	1.8	(16.1)							

%C - Percent Cohesive Failure
* Not included in shear strength average

PAE SO_2 ENVIRONMENTAL EXPOSURE INDIVIDUAL RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

TEST	TEST TEMPERATURE	INITIAL NO EXPOSURE		%C	322K (120°F)/ 95% R.H. 1000 HOURS		%C	STRESSED SKYDROL AT AMBIENT # 1000 HOURS	%C
Lap Shear MPa (psi)	Ambient	26.7	(3870)	75	14.8	(2150)	75		
		22.1	(3200)	50	16.0	(2320)	90		
		21.4	(3098)	60	14.8	(2140)	60	*	
		26.3	(3810)	80	15.4	(2240)	65		
		20.0	(2900)	40	15.4	(2236)	80		
	Avg.	23.3	(2880)		15.3	(2220)			
	450K (350°F)	23.1	(3350)	100	15.6	(2260)	95		
		21.8	(3160)	80	13.9	(2020)	95		
		18.6	(2700)	95	15.7	(2280)	90	*	
		23.8	(3450)	100	13.1	(1900)	95		
		18.6	(2700)	90	14.3	(2084)	90		
	Avg.	21.2	(3070)		14.5	(2110)			
Drum Peel N.M. (in.lb.)	Ambient	2.0	(17.5)	100	2.3	(21.5)	100		
		2.0	(17.5)	100	1.3	(12.0)	100		
		1.6	(13.8)	100	1.5	(13.5)	100		
		1.8	(16.3)	100	2.2	(20.0)	100		
	Avg.	1.8	(16.3)		1.9	(16.8)			

%C - Percent Cohesive Failure

* Three specimens failed after 250 hours.
* Two specimens failed after 320 hours.
* One specimen failed after 380 hours.
* Two specimens failed after 450 hours.
* One specimen failed after 625 hours.

\# - Stressed at 25% of ultimate strength

PAE SO_2 CRACK EXTENSION INDIVIDUAL TEST RESULTS
ADHEREND - 6AL-4V TITANIUM
SURFACE PREPARATION - CHROMIC ACID ANODIZE

EXPOSURE		EXPOSURE TIME (HOURS) 0		500		1000		3000	
		mm	(inches)	mm	(inches)	mm	(inches)	mm	(inches)
Ambient		23.9	(0.94)	24.9	(0.98)	25.1	(0.99)	25.4	(1.00)
		24.1	(0.95)	24.6	(0.97)	24.9	(0.98)	24.9	(0.98)
		23.6	(0.83)	24.4	(0.95)	24.6	(0.97)	25.1	(0.99)
		22.6	(0.89)	24.9	(0.98)	24.9	(0.98)	24.9	(0.98)
	Average	23.6	(0.93)	24.6	(0.97)	24.9	(098)	25.1	(0.99)
450K (350°F)		23.1	(0.91)	24.4	(0.96)	25.3	(0.96)	25.3	(0.96)
		22.1	(0.87)	23.6	(0.93)	23.6	(0.93)	23.6	(0.93)
		22.4	(0.88)	23.4	(0.92)	23.6	(0.93)	23.6	(0.93)
		23.4	(0.92)	23.9	(0.94)	25.3	(0.96)	25.3	(0.96)
	Average	22.6	(0.90)	23.9	(0.94)	23.9	(0.94)	23.9	(0.94)
505K (450°F)		23.6	(0.93)	25.4	(1.00)	26.7	(1.05)	26.7	(1.05)
		24.6	(0.97)	26.7	(1.05)	26.7	(1.05)	26.7	(1.05)
		23.9	(0.94)	25.9	(1.02)	25.9	(1.02)	25.9	(1.02)
		23.6	(0.93)	25.7	(1.01)	25.6	(1.01)	25.6	(1.01)
	Average	23.9	(0.94)	25.9	(1.02)	26.1	(1.03)	26.1	(1.03)
322K (120°F/95% R.H. Tested at Ambient Temperature		23.1	(0.91)	25.4	(1.00)	27.9	(1.10) 1/	—	
		23.4	(0.92)	24.6	(0.97)	27.4	(1.08)	—	
		22.6	(0.89)	24.6	(0.97)	29.0	(1.14)	—	
		24.4	(0.96)	28.2	(1.11)	29.7	(1.17)	—	
	Average	23.4	(0.92)	25.7	(1.01)	28.4	(1.12)	—	
322K (120°F/95% R.H. Tested After 450K (350°F)/10 Min. Exp.		24.4	(0.96)	28.2	(1.11)	27.4	(1.08) 1/	—	
		24.6	(0.97)	27.4	(1.08)	31.5	(1.24)	—	
		24.9	(0.98)	28.4	(1.12)	31.5	(1.24)	—	
		23.1	(0.91)	26.4	(1.04)	28.2	(1.11)	—	
	Average	24.4	(0.96)	27.7	(1.09	29.7	(1.17)	—	

1/ All cohesive failures

LAP-SHEAR PERFORMANCE OF EXPERIMENTAL POLYMERS

ADHEREND - 17-7 PH STAINLESS STEEL
SURFACE PREPARATION - SULFURIC ACID ANODIZE

TEST CONDITION	PPQ MPa	(psi)	% C	STPI/LaRC-2 MPa	(psi)	% C	PAE SO_2 MPa	(psi)
Ambient, Initial	18.6	(2700)	10	24.3	(3520)	30		
	16.6	(2400)	10	24.0	(3480)	40		
	19.7	(2860)	15	29.0	(4200)	100	*	
	17.0	(2470)	25	24.5	(3550)	20		
Average:	18.0	(2610)		25.4	(3690)			
450K (350°F), Initial	12.7	(1840)	0	17.7	(2560)	40		
	14.1	(2040)	5	16.3	(2360)	10		
	14.4	(2090)	25	20.0	(2880)	50	*	
	14.4	(2080)	25	18.1	(2618)	20		
Average:	13.9	(2010)		17.9	(2600)			
505K (450°F), Initial	15.7	(2280)	0	14.1	(2090)	25		
	14.2	(2060)	0	18.8	(2720)	50	*	
	14.2	(2060)	5	15.2	(2204)	10		
	15.8	(2290)	20	3.3	(480)	0		
Average:	15.0	(2170)		12.8	(1850)			
Ambient After Exposure to	1.4	(200)	0	23.8	(3450)	25		
322K (120°F)/95% R.H.,	—	—	0	21.3	(3090)	25	*	
1000 Hours	0.8	(120)	0	19.6	(2840)	5		
	3.0	(430)	0	26.0	(2910)	10		
Average:	1.7	(250)		21.2	(3070)			

* Specimens failed in machining

%C = Percent cohesive failure

Standard Bibliographic Page

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15. Supplementary Notes

NASA Technical Representative - Mr. Paul M. Hergenrother
Final Report

16. Abstract

The evaluation of three experimental polymers from NASA-Langley and a commercially produced polymer from Mitsui Toatsu Chemicals as high temperature structural adhesives is presented. A polyphenylquinoxaline (PPQ), polyimide (STPI/LaRC-2), and a polyarylene ether (PAE-SO_2)were evaluated as metal-to-metal adhesives. Lap shear, crack extension, and climbing drum peel specimens were fabricated from all three polymers and tested after thermal, combined thermal/humidity, and stressed hydraulic fluid (Skydrol) exposure. The fourth polymer, LARC-TPI was evaluated as an adhesive for titanium honeycomb sandwich structure.

All three experimental polymers performed well as metal-to-metal adhesives from 219K (-65° F) to 505K (450°F), including humidity exposure. Structural adhesive strength was also maintained at 505K (450°F) for a minimum of 3,000 hours exposure.

LaRC-TPI was evaluated as a high temperature (505K(450°F))adhesive for titanium honeycomb sandwich structure. The LaRC-TPI bonding process development concentrated on improving the honeycomb core core to skin bond. The most promising approach of those evaluated combined a LaRC-TPI polymer solution with a semi-crystalline LaRC-TPI powder for adhesive film fabrication and fillet formation.

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